EAGLE FORD FRACTURE FLUID OPTIMIZATION USING AVAILABLE NON-POTABLE WATERS

An Undergraduate Research Scholars Thesis

by

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ABSTRACT

Eagle Ford Fracture Fluid Optimization Using Available Non-Potable Waters. (May 2015)

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Water shortage has been a challenge in developing hydraulic fracturing in drought-affected areas such as South (Eagle Ford) and West (Permian Basin) Texas. Non-potable groundwater is a potential alternative to fresh water in making hydraulic fracture fluids. The purpose of this study is to evaluate the technical feasibility of using non-potable waters from the Southern Carrizo-Wilcox aquifer to make hydraulic fracturing fluids in the Eagle Ford play. The first phase of the research is to compare fracture fluid compositional requirements with the water compositions of the Southern Carrizo-Wilcox aquifer by searching through literature, manufacturer's, and service company's specifications. The second phase of the research is to evaluate the performance of two different types of fracture fluids using synthetic saline water in the laboratory. Two major lab experiments will be conducted: (1) using a flow loop system to test for friction reducer performance in slickwater and (2) performing viscosity measurements and "lipping gel" experiments for crosslinked gel performance. After completing literature reviews and laboratory evaluations, a conclusion of the technical feasibility of using non-potable groundwater to make these fracture fluids can be derived. This research will demonstrate the possibility of eliminating the use of fresh water by utilizing the available abundant non-potable groundwater from the Southern Carrizo-Wilcox aquifer in hydraulic fracturing.

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NOMENCLATURE

$[B^{3+}]$	Boron concentration
$[Ba^{2+}]$	Barium concentration
$[Ca^{2+}]$	Calcium concentration
$[Cl^{-}]$	Chloride concentration
$[CO_3^{2-}]$	Carbonate concentration
$[Fe^{2+}]$	Iron concentration
$[HCO_3^{-}]$	Bicarbonate concentration
$[K^{+}]$	Potassium concentration
$[Mg^{2+}]$	Magnesium concentration
$[Na^{+}]$	Sodium Concentration
$[SO_4^{2-}]$	Sulfate concentration
$[Sr^{2+}]$	Strontium concentration
FR	Friction reducer
S C-W	Southern Carrizo-Wilcox
SPE	Society of Petroleum Engineers
TDS	Total Dissolved Solids
TSS	Total Suspended Solids
TWDB	Texas Water Development Board
USGS	United States Geological Survey

CHAPTER I

INTRODUCTION

Unconventional shale gas has played an important key in developing the U.S. energy economy. The combination of horizontal drilling and hydraulic fracturing allows the petroleum industry to produce natural gas economically from low permeability shale plays. The development of shale gas in major shale plays such as Barnett Shale, Eagle Ford Shale, and Haynesville Shale in Texas resulted in a significant increase in hydraulic fracturing jobs in these areas. FracFocus is a website for operators to report their hydraulic fracturing activities voluntarily. According to FracFocus, out of 72,815 reported frac jobs, there are 35,519 frac jobs in Texas and specifically 10,605 frac jobs in the Eagle Ford Shale formation. By using these data, a comparison chart was constructed to show the significant increase in hydraulic fracturing in the Eagle Ford Shale formation as **Fig. 1** in **Appendix A**.

The number of frac jobs in the Eagle Ford Shale formation has increase significantly since 2011 to 2014. It is accounted for more than 20% of fracturing jobs in Texas. Moreover, hydraulic fracturing activities are highly active in Dimmitt, La Salle, and Karnes counties in the Eagle Ford area as shown in **Fig. 2** in **Appendix A**.

The significant increase in hydraulic fracturing has significantly impacted water management in the Eagle Ford area since the major component of hydraulic fracturing fluids is water. Due to the rapid increase of hydraulic fracturing jobs and large volumes of water required for each job, water shortage could become a problem in a drought area like the Eagle Ford Shale formation.

Water Usage in Hydraulic Fracturing and Water Shortage in the Eagle Ford Shale Formation

Fresh water is generally used for making fracture fluids, due to ease of preparing fluids with consistently reliable behavior. Fresh water is withdrawn from surface water sources such rivers, lakes, and municipal supplies or subsurface fresh water aquifers *via* water wells. In Texas, many of the surface water sources are owned and managed by the State and require a water-right permit for industry use (Nicot et al, 2012). Regulations and public attention have become more strict in water use for hydraulic fracturing activities since water shortages are expected to become a problem in water management in a drought region like the Eagle Ford area. Hydraulic fracturing activities require larger volumes of water to make fracture fluid compared to drilling activities as shown in **Table 1** (King, 2012).

Five to ten billion gallons per year of water were used for hydraulic fracturing over 15 years in the Eagle Ford Shale Formation (Clapp et al., 2013). Based on data from a Texas statewide media report (Kluge, 2014)**, t**his amount of fresh water could have been supplied for over 150,000 single and multi-family residences per year**.** According to a Cerus report (Freyman, 2014)**,** the Eagle Ford Shale play has the highest water use in the nation comparing to other major U.S. shale plays such as Marcellus, Permian, Barnett and Haynesville. Moreover, Dimmit County with the largest number of active wells in the Eagle Ford area has the largest volume of water use nationally. Even though the amount of water used in hydraulic fracturing is relative small compared to other industries such as thermoelectric power, irrigation, or public supply, the development of hydraulic fracturing in drought areas can result in a shortage of water. Therefore, operators in the Eagle Ford Shale formation have faced a challenge of finding water supplies

when developing a large number of wells in this region. More than 98% wells in the Eagle Ford area have recently experienced from medium to high water stress (Freyman, 2014). Almost 90% of water used in hydraulic fracturing at the Eagle Ford area is underground water from the Southern Carrizo-Wilcox (S C-W) aquifer (Nicot et al., 2012). However, only 20% of this underground water is brackish water while 80% of it is fresh water to be used in making hydraulic fracturing fluids. Due to the significant increase of shale development in the Eagle Ford Shale formation, the fresh water reserve of the Southern Carrizo-Wilcox aquifer is being significantly depleted. Therefore, finding a sustainable water source for hydraulic fracturing activities in the Eagle Ford area is crucial in continued development of shale gas in this region. The deeper zone of the Southern Carrizo-Wilcox aquifer which contains large volumes of either highly brackish or saline water can be consider as a possible alternative for fresh water.

Previous Research Utilizing Non-Potable Water Sources in Making Fracture Fluids

Since the high salinity of brackish and saline waters may affect the performance of chemicals used in fracturing fluids, it is a challenge to utilize these waters in making fracturing fluids. Several researchers and operators have done extensive research to develop cutting edge technologies in order to utilize water sources with high salinity in making fracturing fluids. Several practices of using water with high salinity such as produced waters to make fracture fluids have been reported in a Cerus Report (Freyman, 2014). Because of the strict regulation of Pennsylvania on using fresh water sources and disposing produced water, the use of high saline water has been practiced actively in the Marcellus play. Many operators such as Apache, Anadarko, Shell, and Chesapeake have recently utilized high saline water in designing their fracture fluids. Moreover, more than 17 publications from the Society of Petroleum Engineers

have reported several successful cases of making different fracturing fluid types using available non-potable water sources. Furthermore, from the report data of FracFocus, there were some attempts of using saline water in making fracture fluid at the Eagle Ford Shale formation. Around 909 wells out of 10,605 wells in the Eagle Ford Shale formation used saline water to make fracture fluids as shown in **Fig. 3** in **Appendix A**.

The Trend of Fracture Fluid Types in the Eagle Ford Shale Formation

Several different fracture treatment types such as crosslinked gel, slickwater, hybrid, energized, acid frac, gas frac, and matrix acidizing have been practiced in the industry (Robart et al., 2013). Based on different characteristics of the formation, different fracture treatment types will result in different production responses. Therefore, it is important to investigate what type of fracturing fluids has been used at the Eagle Ford formation and analyze the makeup water composition limitations of different fracture fluid types. A recent SPE 163875 article published by PacWest Consulting Partners has done an intensive analysis about hydraulic fracturing fluid system trends in the U.S. based on available data from the FracFocus website. By using published chemical disclosure data of every fracturing job in the U.S from the FracFocus website, PacWest Consulting Partners was able to determine the fracture fluid type used in every fracturing job at several major shale formation regions of the U.S. According to the study of PacWest Consulting Partners, the three most common fracture fluid types being used at the Eagle Ford formation are slickwater (SW), cross-linked gel (XL), and hybrid (XL/SW) fracture fluids as shown in **Fig. 4** in **Appendix A** (PacWest, 2014). The dominant fracture fluid type is hybrid fracture fluid which is utilized by 54% of the total of fractured wells. **Fig. 5** in **Appendix A** shows that hybrid fracture fluids (slickwater followed by gelled fluids) have been favorable at the Eagle Ford Shale

formation for several years, and it is followed by crosslinked gel and slickwater. However, there has been a dramatic increase in using slickwater in this region recently. According to the PacWest analysis, slickwater will continue increasing from 11% in 2013 to 28% in 2016 due to its cost efficiency.

Research Objectives

Several operators in the Eagle Ford area have taken an initial step in utilizing brackish water in making fracturing fluids. However, a large amount of fresh water is still being used to make fracture fluids. The fresh water sources are being depleted due to the shale gas development. Therefore, it is crucial to reduce the use of fresh water by utilizing non-potable waters from the deeper portions of the Southern Carrizo-Wilcox aquifer in making fracturing fluids. However, a thorough study is needed to prove that it is practicable to utilize these water sources in the Eagle Ford area. Utilization of non-potable water to make fracture fluids still faces many challenges since these waters contain much higher salinity and ions than fresh water. High concentration of anions such as CO_3^{2-}, SO_4^{2-}, S^{2-} in these waters may cause the precipitation of divalent metal ions like Ca^{2+}, Fe^{2+}, Ba^{2+}, and Sr^{2+} when interacting with the formation fluid. These same divalent ions or high total salinity might affect the performance of some chemical components which are initially designed for best use in fresh water. For example, monovalent and divalent cation ions affect the hydration of guar polymers to produce high viscosity linear polymer solutions and crosslinked gels. They can also reduce the performance of friction reducer in slickwater. High bacteria concentrations in these waters can further cause damage to facility equipment. High total suspended solids (TSS) and organic compounds in non-potable waters can result in formation damage due to blockage of pores. High concentration of iron can cause the

decrease of scale inhibitors' performance. There are two approaches to solve these problems. Firstly, expensive chemicals that are not degraded under these conditions can be used in making fracture fluids. There is an association between the cost of the chemicals and the salinity tolerance of these chemicals. The second approach is to use an economical water treatment to decrease loading of undesirable components to make these water sources practical for use in making fracture fluids. However, it is a challenging to clean these waters close to fresh water quality. More advanced technology will be required, but it can increase the cost of using these waters. Therefore, understanding the limitations of water composition of different fracture fluids types and their properties will be essential to analyze and optimize the cost effectiveness of different methods. Developing this understanding is the purpose of this study.

CHAPTER II

METHODS

Observed Water Composition Limitations of Different Fracture Fluid Types in Multiple Studies in SPE Literature and Company Product Specifications

More than 17 publications from the Society of Petroleum Engineers have reported several successful cases of making different fracturing fluid types in a laboratory or field using available non-potable water sources as summarized in **Table 2** in **Appendix A**.

The makeup water composition of the testing fluids reported in these SPE articles are useful resources to analyze the limitations of makeup water composition of different fracture fluid types. However, since each study was performed under different conditions, they have different observed makeup water composition. These observed results demonstrate how high salinity of makeup water can be tolerated in making different fracture fluids. They are not necessarily upper limits of makeup water composition. Therefore, a verification of water composition limitations in a lab is required to find the upper limit of water composition.

Another useful resources for analyzing makeup water composition limitations is to use company product specifications. Some service companies such as Schlumberger or Halliburton have developed new fracture fluid systems which allow the industry to make fracture fluids from non-potable waters. Moreover, some chemical companies such as SNF or Chem Rock Technologies have introduced their commercial friction reducer products with tolerance of high salinity. By

verifying these companies' product specifications, we can show that current commercial products are allowed to be used in non-potable waters with high salinity.

From the groundwater database of Texas Water Development Board (TWDB), a data of groundwater composition were obtained to compare with the water composition limitations from SPE literature review. According to United States Geological Survey, groundwater is divided into four water types as shown in **Table 3** in **Appendix A** (USGS, 2014).

By using these definitions, non-potable water was defined as slightly saline water, moderately saline water, and highly saline water. 750 out of 8,989 water sample data from TWDB database of the South Texas/Eagle Ford region are from non-potable water wells. This data includes TDS, Na^+, K^+, Ca^{2+}, Mg^{2+}, Sr^{2+}, Cl^-, SO_4^{2-}, CO_3^{2-}, and HCO_3^- concentrations of groundwater samples from the Southern Carrizo-Wilcox aquifer. The data of Ba^{2+}, B^{3+}, and Fe^{2+} used in this study are separate from that data set, and take into account the groundwater samples from the entire Carrizo-Wilcox aquifer. @RISK software were used to determine the P10, P50, P90, and MAX values which are define as the following:

- P10: 10 % of the total non-potable water well samples have the ion concentration less than or equal to this value.
    - For example, if P10 of Ca^{2+} concentration of Southern Carrizo-Wilcox groundwater composition is 500 ppm, it means that 10% of the total water samples has Ca^{2+} concentration lower than or equal to 500 ppm.
- P50: 50 % of the total non-potable water well samples have the ion concentration less than or equal to this value.

- P90: 90 % of the total non-potable water well samples have the ion concentration less than or equal to this value.
- MAX: the maximum ion concentration of Southern Carrizo-Wilcox groundwater composition in the database.

Laboratory Evaluation of Water Composition Limitations for Slickwater and Borate-crosslinked Guar Gel

After compiling the water composition maxima for different fracture fluids types, these literature salinity limitations will be compared to Southern Carrizo-Wilcox groundwater and performance of fracture fluids up to maximum salinities of the Southern Carrizo-Wilcox or company-specified upper limits (if lower than S C-W maximum salinities). Performance in brines of Southern Carrizo-Wilcox composition will be verified with laboratory experiments. The first experiment is to verify the properties of slickwater using saline aquifer water. Friction reducer is the main additive of slickwater that is significantly affected by the salinity level of makeup water. A flow loop test is designed and constructed to analyze the effectiveness of friction reducers used in saline water. A commercial anionic friction reducer was obtained from a chemical company. The main objective of this test is to determine degree of friction reduction in natural or synthetic Southern Carrizo-Wilcox aquifer brine (at highest salinity expected for source water wells) compared to performance in fresh water. The synthetic saline water used in this experiment was made up of the maximum concentration of all ions and 10 ppm Fe^{2+}. Second experiment is to verify fracture fluid properties of cross-linked borate guar/borate gel using salinity aquifer. For testing the performance of linear guar polymer in natural or synthetic Southern Carrizo-Wilcox aquifer brine (at highest salinity expected for source water) compared to fresh water, rheology

tests are performed by using the Brookfield DV-III Ultra Programmable Rheometer to measure viscosity of the testing fluids. For analyzing the performance of cross-linked guar/borate gels in natural or synthetic Southern Carrizo-Wilcox aquifer brine compared to fresh water, “lipping gel” qualitative experiments are used to determine the strength of this fluid.

Based on the comparison between the water composition of the S C-W groundwater and observed water composition limitations of different fracture fluid types in multiple studies in SPE literature, six laboratory experiment scenarios were developed to verify the technical feasibility of using S C-W groundwater to make fracture fluids.

- Case 1: Fresh water + 3000ppm Guar
- Case 2: Max. concentration of all ions + 368ppm Fe^{2+} + 3000ppm Guar
- Case 3: Max. concentration of all ions excluding Fe^{2+} + 3000ppm Guar
- Case 4: Max. concentration of all monovalent ions excluding divalent and Fe^{2+} ions + +3000ppm Guar
- Case 5: P90 values of all ions + 10ppm Fe^{2+} + 3000ppm Guar
- Case 6: Max. concentration of all ions excluding Fe^{2+} + 6000ppm Guar

Since the concentration of barium is relatively low compared to other ions present in groundwater, in order to ease the weighting procedure, 40 ppm of barium were used in making synthetic saline water for Case 2 to Case 6. Boron was not used in making synthetic saline water since its concentration in groundwater is small, less than 6 ppm.

Lab Procedures for Testing the Performance of Friction Reducer in Saline Water

Equipment

- A positive displacement, low-shear pump (Capacity: up to 11.23 gpm)
- 10’ long hose with OD ¾”
- A tank (reservoir): 30 L capacity
- A pressure gauge or a differential pressure transducer
- A magnetic flow meter
- Optional: A mass flow meter
- A mixer

Flow Loop Diagram and Equipment

A specific flow loop was designed to measure frictional pressure drop of the fluid as shown in **Fig. 6** and **Fig. 7** in **Appendix A.**

Chemicals

- Water (distilled water preferred but not essential) , CAS# 7732-18-5
- NaCl, CAS# 7647-14-5
- KCl, CAS# 7447-40-7
- $CaCl_2$, CAS# 7440-70-2
- $MgCl_2$, CAS# 7786-30-3
- $FeCl_3$, CAS# 7705-08-0
- $Ba(NO_3)_2$, CAS# 10022-31-8
- Anionic friction reducer, CAS# 64742-47-8

Procedures

Preparation of synthetic saline water

- Measure 3 L of warm water in a 3L beaker
- Heat the water at 50^{o}C while stirring it at 400 RPM
- Add the required amount of salt for 18 L based on **Table 4** and **Table 5** in **Appendix A** to the water
- Allow the solution become clear

Measure Pressure Drop of the Base Fluid and the Fluid with Friction Reducer

- Make sure the shut-off valve below the reservoir (valve 1) closed so that the water does not enter into the flow loop system
- Fill the tank with 18 L of tap water if testing the performance of friction reducer in fresh water or 15 L of tap water and 3 L of prepared synthetic water if testing the performance of friction reducer in synthetic water
- Check and calibrate the flow meter and pressure transducers
- Open all the shut-off valves to allow the fluid to enter the flow loop system
- Turn the pump on and establish the flow rate at 11 gpm
- Circulate the base fluid for 5 minutes or until the pressure drop stabilize
- Record the pressure drop when they stabilize.
- Prepare the 1ppt friction reducer by taking a 500 mL sample of the base fluid from the tank into a beaker and add 18mL of the friction reducer to the fluid while mixing the fluid at 300 RPM as shown in **Fig. 8** in **Appendix A**
- Allow the friction reducer to fully hydrate

- Add the friction reducer into the flow loop system with the base fluid circulating
- Circulate the base fluid for 5 minutes or until the pressure drop stabilize
- Record the pressure drop when they stabilize.
- After finishing the test, turn off the pump and then drain the water out of the system using the required disposal method.

Calculation of Friction Reduction

- Calculate Friction Reduction by using the following equation:

$$\%FR = \frac{\Delta P_{BaseFluid} - \Delta P_{Solution}}{\Delta P_{BaseFluid}} \quad (1)$$

Lab Procedures for Testing the Performance of Borate-crosslinked Guar Gel

Equipment

- Waring blender
- Rheostat
- Pipette (if pipette is unavailable, use syringes)
- 100 graduated cylinder
- A 250mL beaker
- 2 500mL beakers
- Top loading balance
- A magnetic stirrer with a hot plate

Chemicals

- Water (distilled water preferred but not essential) , CAS# 7732-18-5
- J580 Guar Gum, CAS# 9000-30-0
- Sodium Tetraborate (borax), CAS# 1330-43-4
- Ethylene Glycol, CAS# 107-21-1
- NaOH 50% solution, CAS# 1310-73-2
- NaCl, CAS# 7647-14-5
- KCl, CAS# 7447-40-7
- $CaCl_2$, CAS# 7440-70-2
- $MgCl_2$, CAS# 7786-30-3
- $FeCl_3$, CAS# 7705-08-0
- $Ba(NO_3)_2$, CAS# 10022-31-8

Procedures

Preparation of an activator NaOH 30% solution

- Fill a 250 mL beaker with 40 mL of water
- Stir the water at the rate of 200 RPM while heating it at 50^{o}C
- Measure and add 60 grams of the NaOH 50% solution slowly to the water
- Wait until a clear solution is obtained
- Remove the beaker from the heat and allow it to cool.
- Pour the solution into a properly labeled bottle with a sealed cap.

Preparation of a crosslinker 5% borax solution

- Fill a 250 mL beaker with 55 mL of water
- Measure and add 5 grams of borax to the water with stirring at 400 RPM
- Heat the mixture at 50^{o}C while stirring and allow the borax dissolved completely in water. Avoid boiling the solution
- After obtaining a clear solution, measure and add 40 grams of ethylene glycol to the solution. Wait until the solution become homogenous
- Remove the beaker from the heat and allow it to cool.
- Pour the solution into a properly labeled bottle with a sealed cap.

Preparation of synthetic saline water

- Measure 1.5 L of warm water in a 3L beaker
- Heat the water at 50^{o}C with stirring at 400 RPM
- Add the required amount of salt based on **Table 4** and **Table 5 in Appendix A** to the water
- Allow the solution become clear

Preparation of borate-crosslinked guar gel

- Put 500 mL of base water (either tap water or prepared synthetic saline water) in the blender as shown in **Fig. 9** in **Appendix A**
- Adjust the rheostat to create enough shear (vortex)
- Add 1.5 grams of J580 to the solution and allow it mixed and hydrated for 10 minutes

- Take a small sample of this linear guar solution to measure its viscosity by using the Brookfield DV-III Ultra Programmable Rheometer with the LV1 spindle as **Fig. 10** in **Appendix A**
- Make sure to keep the blender running while measuring the viscosity of the linear guar
- After finishing measuring the viscosity of the linear guar, pour the sample back to the mixer
- Add 1.9 mL of the activator to the solution and allow it mix for 1-2 minutes
- Add 2.84 mL of the crosslinker to the solution and allow it crosslinks for at least 2 minutes
- Pour the gel to a 500 mL beaker and continue to pour it from beaker to beaker for at least 10 times
- Leave the gel in the beaker for 5-10 minutes and then observe the lipping characteristic by leaning the container to it side and tip it back as shown in **Fig. 11** in **Appendix A**. The gel should retract back into the beaker.

CHAPTER III

RESULTS

Observed Water Composition Limitations of Different Fracture Fluid Types in Multiple Studies in SPE Literature and Company Product Specifications

By looking at a various studies in SPE literature summarized in **Table 2**, the make-up water composition of different fracture fluid types from multiple successful cases is observed and recorded in **Table 6**. Based on this table, we can conclude that crosslinked gel is not affected greatly by salinity level and can be made from waters with high salinity. Borate-crosslinked guar fracture fluids can be made from waters with TDS up to over 130k ppm and Ca^{2+} of over 6000 ppm. Zirconate-crosslinked guar fracture fluids can be made from waters with TDS up to 300k ppm and Ca^{2+} of over 28k ppm. For slickwater fracture fluids, the observed limits of water composition of different studies are varied. Since friction reducer is highly affected by salinity level, different types of friction reducers have different salinity tolerance. For example, anion friction reducers often have lower salinity tolerance than cation and nonionic friction reducers. New commercial friction reducers have higher salinity tolerance than conventional friction reducers. Indeed, some friction reducer products of SNF are designed to be used in high saline water as shown in **Fig. 12** and **Fig. 13** in **Appendix A** (SNF, 2014). More examples of high performance friction reducers are FR-76 of Halliburton and FR-1204 of Chem Rock Technologies. FR-76 of Halliburton can be used effectively in brines with TDS up to 50,000 ppm (Halliburton, 2014). FR-1204 of Chem Rock Technologies can deal with waters with TDS up to 60,000 ppm, allowing for frac/produced water reuse (Chem Rock Technologies, 2014).

By using @RISK software to analyze the groundwater data from the TWDB database, statistics of Southern Carrizo-Wilcox groundwater composition were obtained as shown in **Table 7**. All the P10, P50, P90, and MAX values of TDS and ion concentrations obtained from the statistical analysis were used to compare the observed limitations from several successful case studies in SPE literature in **Table 6**. Analyzing the scatterplots showing these comparisons **helps** to identify the potential ions that may cause problems in making fracture fluids using saline water.

For crosslinked gels, **Fig. 14**, **Fig. 15**, **Fig. 19**, and **Fig. 23** in **Appendix A** shows that P90 values of TDS, sodium, magnesium, and chloride of S C-W aquifer groundwater are much lower than ones of water samples from the case studies in SPE literature. It demonstrates that 90% of non-potable water wells which has the concentration of TDS, sodium, magnesium, and chloride meet the requirements of water composition to make crosslinked gels. However, the maximum concentration values of TDS, sodium, magnesium, and chloride are higher than some of the observed values from SPE literature results. Therefore, a lab evaluation will be useful to verify whether the maximum concentration of these ions will cause any problem in making crosslinked gel. **Fig. 16** and **Fig. 20** in **Appendix A** shows that potassium and strontium concentration of S C-W aquifer water is much less than the potassium and strontium concentration in water sources which people successfully used to make fracture fluids in a laboratory or a field. Therefore, potassium and strontium can be negligible in this study. **Fig. 17** in **Appendix A** shows both of P90 and maximum calcium concentration values of S C-W aquifer is higher than some of the observed limitations from SPE literature. Therefore, calcium can be one of the potential ions causing problems in making fracture fluids from saline waters. **Fig. 18** and **Fig. 22** in **Appendix A** show that the concentrations of barium and boron in groundwater are very small, and many

case studies do not analyze the concentration of these two ions. Hence, these two ions can be negligible in these studies. **Fig. 21** in **Appendix A** shows the P10, P50, P90, and maximum values of iron concentrations in C-W aquifer are higher than some of the iron concentration values from case studies in SPE literature. Therefore, the graph of comparison is scattered. It indicates that iron concentration can be a major problem in making fracture fluids. **Fig. 24** and **Fig. 26** in **Appendix A** shows that the sulfate and bicarbonate concentration of C-W aquifer lies in the region of the observed sulfate and bicarbonate values of case studies from SPE literature. Therefore, these two ions can be a potential problem if their concentrations reach to a certain level. However, if the water is high in divalent cation, the presentation of these ions is relatively small. Hence, in this study, we did not concentrate on experimenting the effect of these ions in making fracture fluids. From SPE literature review based on **Fig. 25** in **Appendix A**, there is not enough sufficient data on the carbonate concentration of water sources used in case studies in SPE literature. Therefore, the assumptions that can be made here are that carbonate does not have a significant impact in making fracture fluids or its concentration in the water sources are relatively small. In conclusion, we determined that the amount of TDS, sodium, calcium, magnesium, chloride, sulfate, and bicarbonate in C-W aquifer water can potentially cause problems in making fracture fluids. However, since the chloride concentration is proportional to the amount of cation in groundwater, and the amount of sulfate, carbonate, and bicarbonate present in goundwater is insignificant if there is a present of divalent cation ions, we did not consider these ions in our study. The iron concentration of C-W aquifer water can be a major problem since the iron concentration of C-W aquifer is crossing all the observed iron concentration values of successful case studies. Therefore, the lab evaluation will be valuable in

verifying the technical feasibility of using C-W aquifer water and determining the major ion causing problems in making fracture fluids.

For slickwater, all the scatter plots from **Fig. 14** to **Fig. 26** in **Appendix A** show that the water composition of Southern Carrizo – Wilcox aquifer is below the observed ion limitations from SPE literature review for most of the ions except iron, sulfate, carbonate, and bicarbonate. Therefore, the potential of using S C-W aquifer to make slickwater is realistic and reliable if S C-W aquifer has a small concentration of iron, sulfate, carbonate, and bicarbonate. A laboratory evaluation for this hypothesis is required.

Laboratory Evaluation of Water Composition Limitations for Slickwater and Borate-crosslinked Guar Gel

Testing the Performance of Friction Reducer in Saline Water

From the **Table 8**, the results indicate that the average friction reduction in fresh water is around 32.53%, and the average friction reduction in the synthetic saline water with TDS of 29,577 ppm is 29.64%. By comparing these two results, we can conclude that the salinity level of S C-W aquifer does not significantly affect the performance of friction reducer. This conclusion is consistent with our results from literature review.

Testing the Performance of borate-crosslinked guar gel

The measurement of viscosity of linear guar in **Fig. 27** in **Appendix A** demonstrates that the salinity level of S C-W aquifer water affects the viscosity of linear guar significantly. The P90 salinity concentration reduces the viscosity of the linear guar less than 15-20 cP. However, the

increase in the amount of monovalent and divalent after P90 salinity values does not significantly reduce the viscosity of the linear guar. This type of experiment allows us to verify the effect of salinity to the performance of the linear guar.

After crosslinking the linear guar, several testing cases were successful in making a good gel from saline water in comparison with fresh water as shown in **Table 9**. We used case 1 of fresh water as a reference to quantitatively compare the gel strength of different testing cases. We identified the strength of the gel using fresh water in **Fig. 28** in **Appendix A** strong. For case 2, when we used the maximum concentration of iron, we could not crosslink the linear guar. The solution after was not considered a gel as shown in **Fig. 29** in **Appendix A**. Therefore, iron and high salinity levels are determined to cause the linear gel not crosslinking. For case 3, we tested the maximum concentration of all ions excluding iron. The linear gel was crosslinked by borax solution. However, the gel is very weak, and the lipping test failed as shown in **Fig. 30** in **Appendix A**. When we compared this case with case 4 in which we successfully made a good gel using synthetic saline water with the maximum concentration of monovalent without divalent and iron as shown in **Fig. 31** in **Appendix A**, we can conclude that divalent ions reduce the performance of the borax solution in crosslinking the linear guar. The success of using synthetic saline water with P90 values of all ions and 10 ppm of Iron in **Fig. 32** in **Appendix A** has demonstrated that 90% of available non-potable wells in the Eagle Ford region can be used to make a good crosslinked gel. The experiment of case 6 as shown in **Fig. 33** in **Appendix A** has shown that increasing the concentration of guar in making crosslinked gel can overcome the problem of high divalent cation concentration in water and make a very strong gel.

CHAPTER IV

CONCLUSIONS

Technical Feasibility of Using Non-potable Waters from the Southern Carrizo-Wilcox Aquifer to Make Different Fracture Fluids

- Literature review shows that the Southern Carrizo-Wilcox aquifer can be used to make fracture fluids since many of its ion concentrations are much lower than the ion concentrations of water samples used in several successful case studies in SPE literature.
- 90% of available non-potable wells of the South C-W aquifer can be used to make crosslinked gel
- The salinity concentration of groundwater from S C-W aquifer does not significantly affect the performance of a commercial friction reducer

Determination of Ions that Potentially Cause Problems in Making Fracture Fluids

- The presence of divalent cations such as Ca^{2+}, Mg^{2+}, or Ba^{2+} at a certain level can cause the crosslinking problem in making crosslinked gels. Increasing the amount of guar used in making crosslinked gels can overcome this problem and produce a good gel.
- The present of iron in saline water can prevent the borax solution to crosslink the linear guar. An economical method is required to treat iron before using saline water to make fracture fluids.

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APPENDIX A

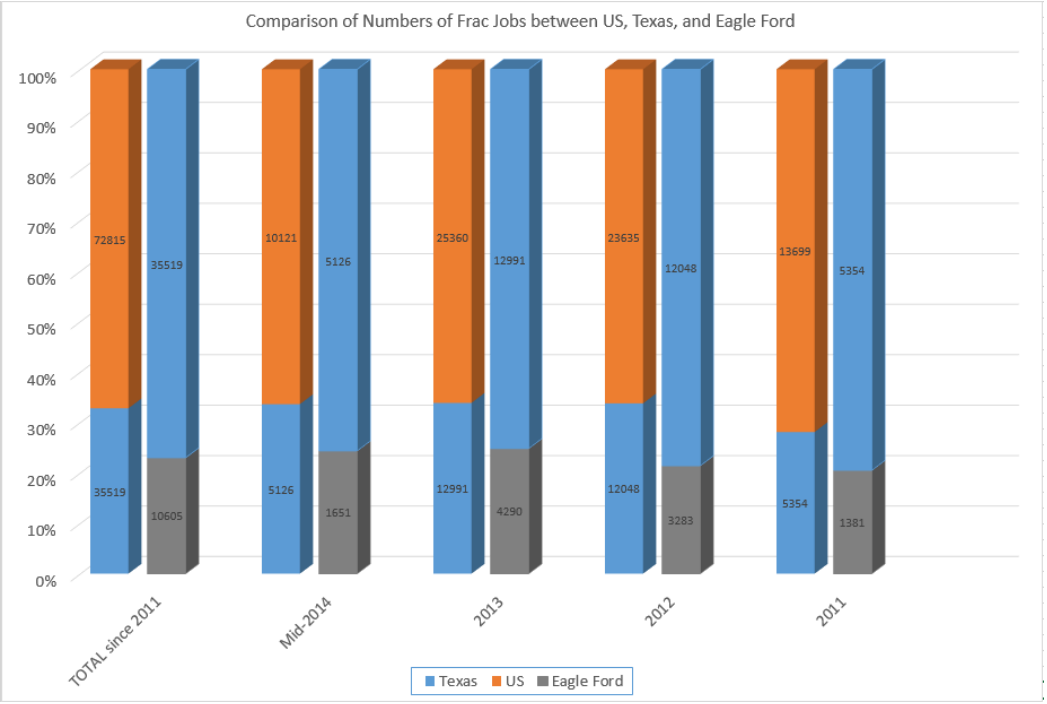

Figure 1 – Comparison of Numbers of Frac Jobs between the U.S., Texas, and Eagle Ford

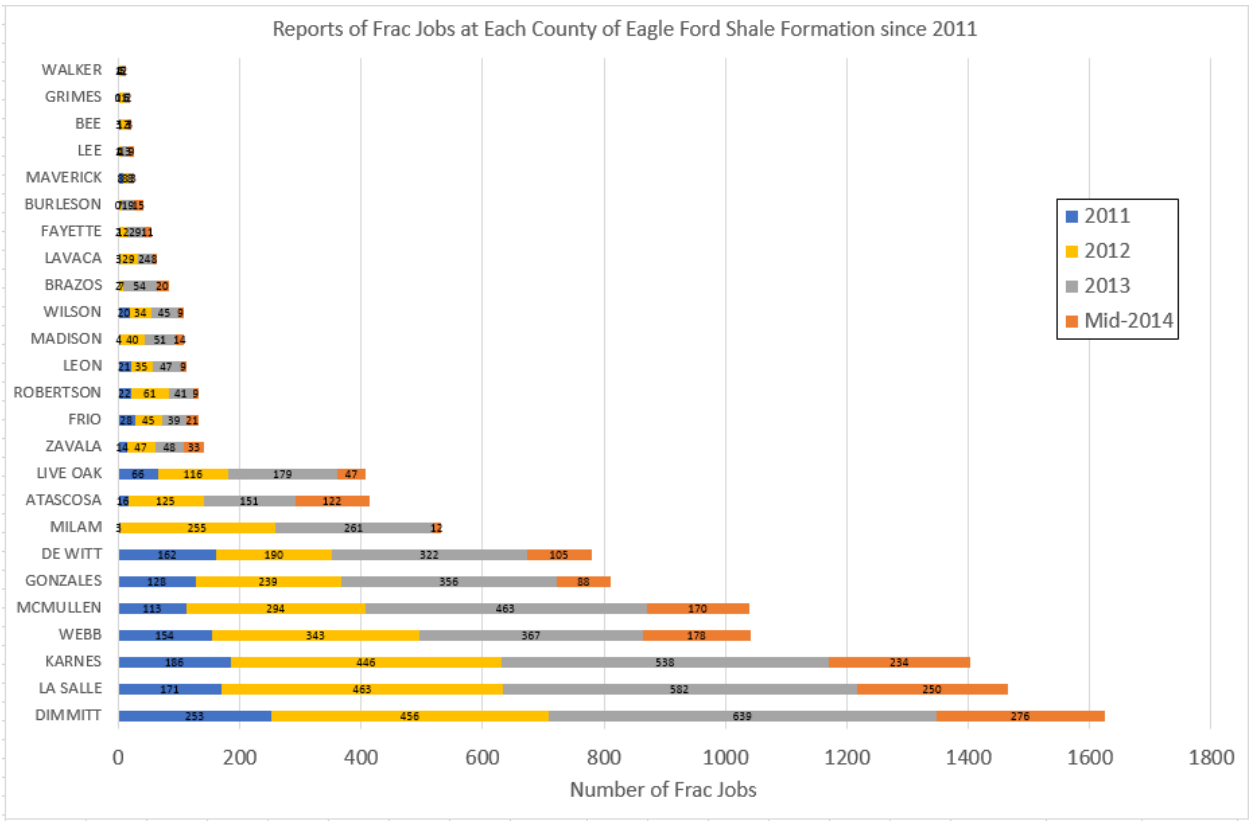

Figure 2 – Number of frac jobs at each county of the Eagle Ford Shale formation since 2011

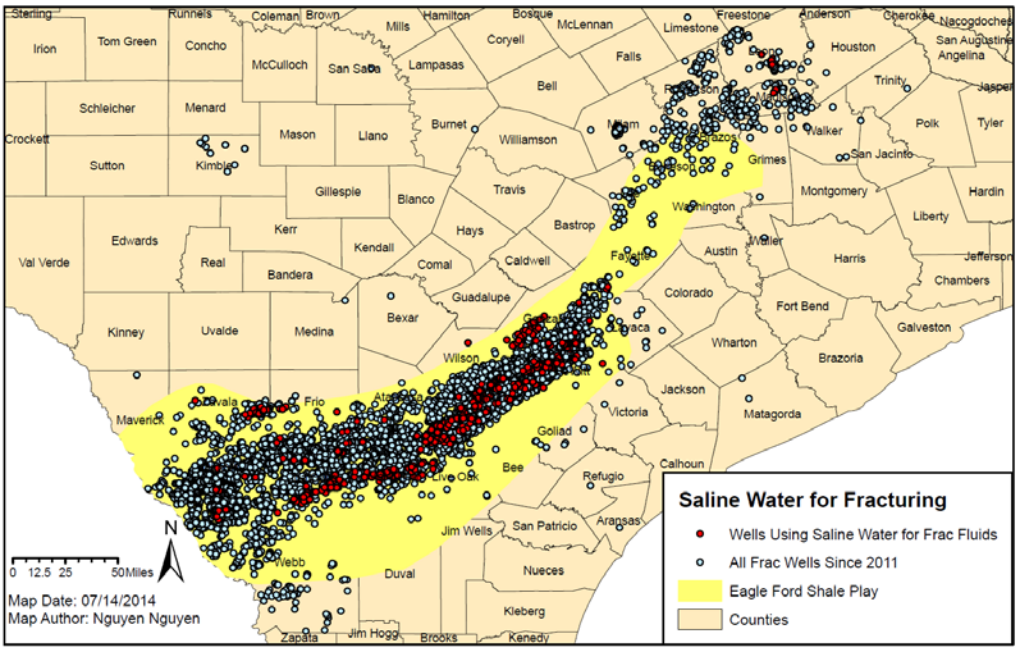

Figure 3 – The use of saline water in the Eagle Ford Shale formation

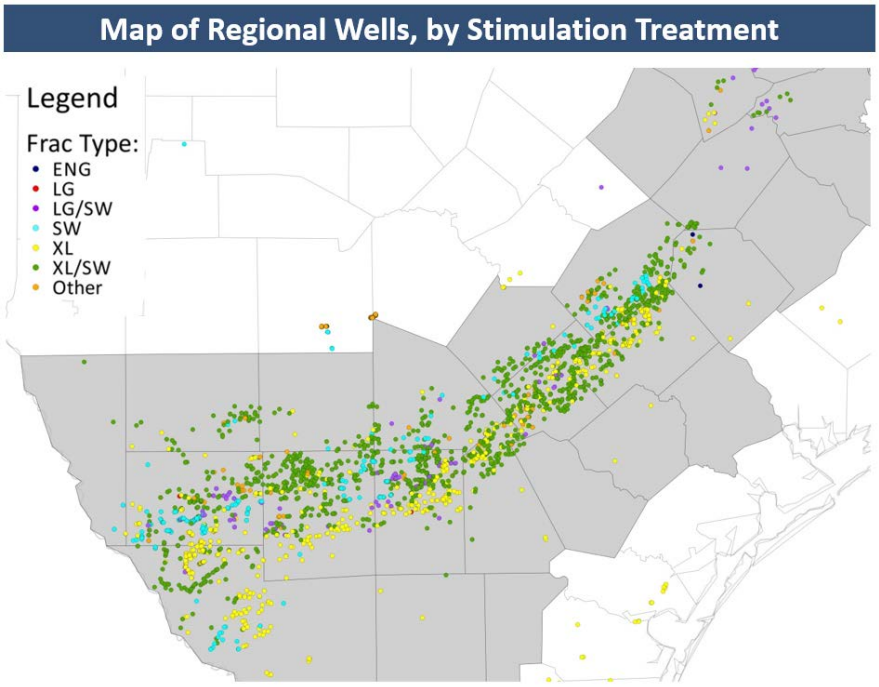

Figure 4 – The map of fracture fluid types in 2013 at the Eagle Ford Shale formation from PacWest
* Personal communication with R. Carbrey. 2014. PacWest Consulting Partners

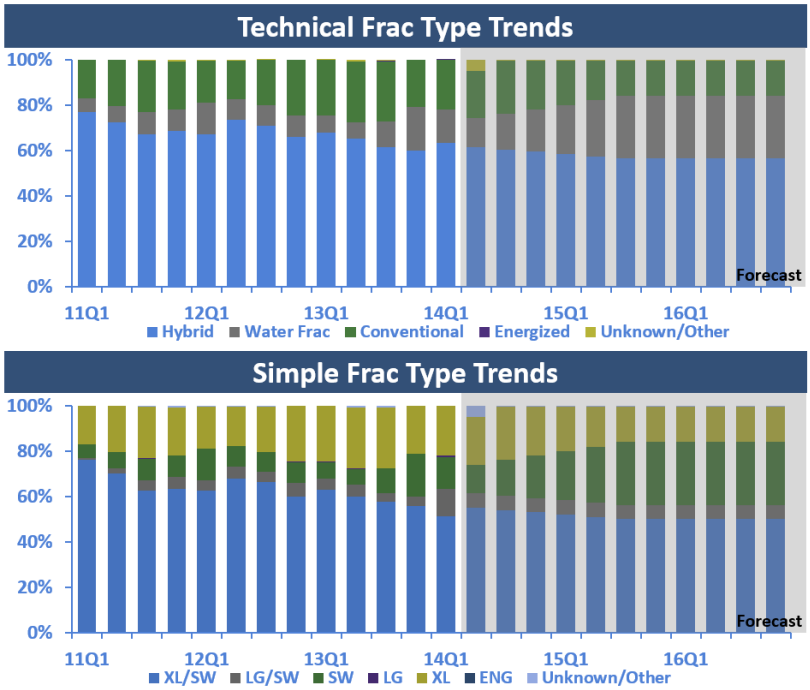

Figure 5 – The trend of fracture fluid types at the Eagle Ford Shale formation from PacWest
* Personal communication with R. Carbrey. 2014. PacWest Consulting Partners

Table 1 – Average volumes of water used per shale well for drilling and fracturing

Unconventional Development	Average Fresh Water Volume for Drilling	Average Fresh Water Volume for Fracturing	Average Salt Water Volume for Fracturing
Barnett	250,000 gallons	4,600,000 gallons	
Eagle Ford	125,000 gallons	5,000,000 gallons	
Haynesville	600,000 gallons	5,000,000 gallons	
Marcellus	85,000 gallons	5,600,000 gallons	Increasing
Niobrara	300,000 gallons	3,000,000 gallons	
Horn River (EnCana and Apache)	250,000 gallons	negligible	Up to 12,000,000 gallons

Table 2 - Successful cases reported in SPE literature of utilizing non-potable waters to make fracture fluids

Article	Type of Fracture Fluid	Lab/Field Scale	Water Source	Field Testing Results (if applicable)
SPE 50777	Borate crosslinked guar	Field	Seawater from Danish North Sea, Offshore Angola, South China Sea, Gulf of Mexico, GOM Formation	Successful using seawater to produce borate-crosslinked guar fluid in the field Danish North Sea, Offshore Angola, South China Sea, Gulf of Mexico, GOM Formation
SPE 25463	Borate crosslinked guar	Lab	Unknown	N/A
SPE 168192	Gel New type alternate viscosifying polymer comparing with Borate-crosslinked guar and CMHPG	Lab	Synthetic seawater with TDS of 35k ppm, and EC Treated produced water from Oil well in Tarrant County Texas with TDS of 110k ppm	N/A
SPE 168614	Borate crosslinked guar	Lab	36 flowback from West Texas region	N/A
SPE 167275	Zirconate crosslinked CMHPG	Lab/ Field	Produced water from Bakken with TDS> 300k ppm, hardness>30k ppm, Boron>500 ppm	A successful two-well trial in the Bakken formation with a total of 52 fracturing stages using 100% untreated produced water

Table 2 continued…

SPE 163824	Zirconate crosslinked CMHPG	Lab/ Field	High-TDS produced water from a Brushy Canyon producing well near Carlsbad, New Mexico; and its treated water with EC	A successful seven-well field trial in XTO's Nash Daw (ND) field in Eddy County, New Mexico with a total of 97 fracturing stages
SPE 167033	Zirconate crosslinked CMHPG	Lab	High TDS produced water	N/A
SPE 94320	Zirconate-crosslinked CMHPG (30%w) and CO2 foamed (70%w)	Lab/ Field	Untreated produced water from a gas-producing well near Aztec, NM	A successful field trial in Township 28 North and Range 11 West of the Dakota formation, San Juan Country, NM.
SPE 121719	Slickwater with Fast-Inverting Friction Reducers	Lab	Produced water from 2 representative wells	N/A
SPE 167775	Slickwater with New Water-based Friction Reducer	Lab/ Field	Produced water with TDS of 300k ppm and $CaCO_3$ over 90k ppm	A successful field test in the lower Bushy Canyon formation located in New Mexico with 17 fracture stages
SPE 168115	Slickwater with slurried powder and powder polyacrylamide	Lab	Sea water 35k ppm produced water 158k ppm	N/A
SPE 164535	Slickwater with a dispersion polymer friction reducer	Lab/ Field	produced water from Marcellus Shale	An operator saved $2.5 MM by using the new fracture fluid system using produced water
SPE 125336	Slickwater with different friction reducers (A, B, and C)	Lab	flowback from Piceance Basin Flowback Sample	N/A
SPE 159837	Slickwater with polyampholytes	Lab	Bakken and Marcellus formation water	N/A
SPE 164493	Slickwater with high brine-tolerant anionic friction reducer C	Lab	hard surface water, produced water, and flowback water	N/A
SPE 144210	Slickwater with different friction reducer (C and D)	Lab/ Field	Flowback and produced water from Horn River and Marcellus	Two successful field trials with FR C in Horn River Shale formation located in Northern British Columbia
SPE 165641	Slickwater with different friction reducers (FR1 and FR2)	Lab	produced water	N/A

Table 3 – Definition of four groundwater types

Water Type	Total Dissolved Solids (TDS) Range
Fresh Water	Less than 1000 ppm
Slightly Saline Water	1,000 ppm to 3,000 ppm
Moderately Saline Water	3,000 ppm to 10,000 ppm
Highly Saline Water	10,000 ppm to 35,000 ppm

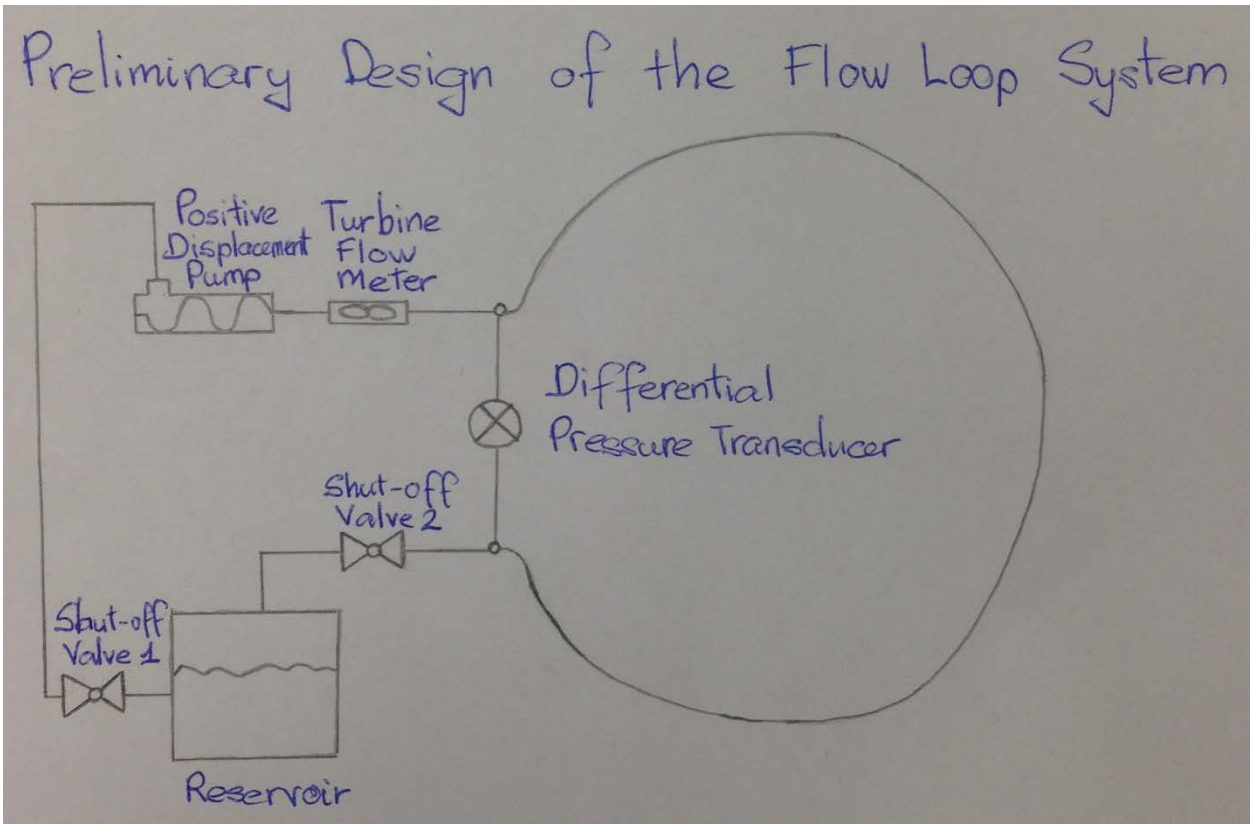

Figure 6 – Flow loop diagram for testing the performance of friction reducer of slickwater

Figure 7 – A completed flow loop system

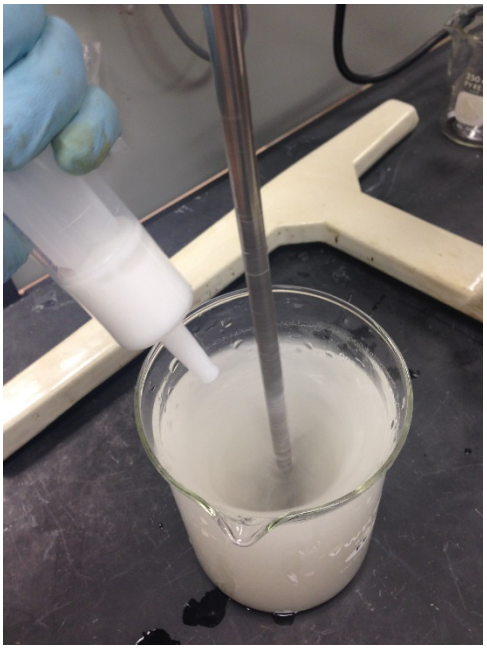

Figure 8 – Inversion procedure of friction reducers

Table 4 – Required amount of salts for the maximum ion concentration of synthetic water

MAX		
Compounds	**Weight/ 1.5 L, g**	**Weight/18L, g**
NaCl	36.704	440.447
$CaCl_2$	4.104	49.246
$Ba(NO_3)_2$	0.114	1.370
KCl	0.383	4.599
$MgCl_2$*6H2O	6.437	77.238
$FeCl_3$	1.603	19.241

Table 5 – Required amount of salts for the P90 values of the ion concentration of synthetic water

P90		
Compounds	**Weight/ 1.5 L, g**	**Weight/18L, g**
NaCl	3.851	46.214
$CaCl_2$	1.196	14.355
$Ba(NO_3)_2$	0.114	1.370
KCl	0.043	0.515
$MgCl_2$*6H2O	1.041	12.497
$FeCl_3$	0.044	0.523

Figure 9 – Mixing the saline solution using a blender with a rheostat

Figure 10 – Measuring linear guar performance using the Brookfild DV-III Ultra Programmable Rheometer with a spindle LV1

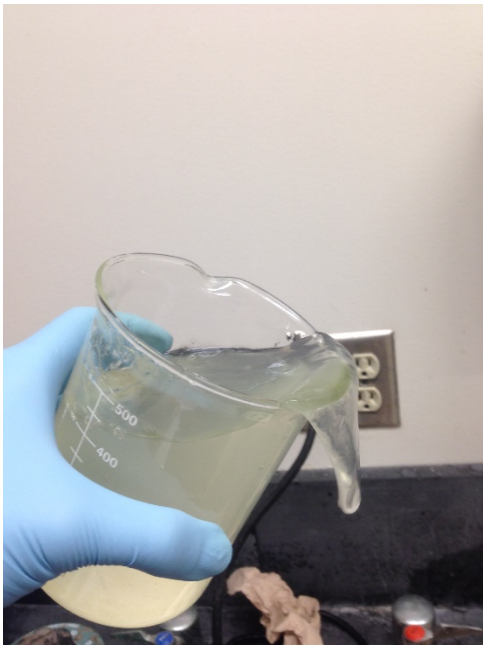

Figure 11 – Lipping Test

Table 6 - Limits Observed in Multiple Studies in SPE Literature for Different Fracture Fluid Types

Contents	Observed Make-up Water Composition for Borate-Crosslinked Guar Fluid, ppm	Observed Make-up Water Composition for Zirconate-Crosslinked Guar Fluid, ppm	Observed Make-up Water Composition for Slick water, ppm
Total Suspended Solids (TSS) Present in Make-up Water in Various Studies	---	**92** [8]	< 100[11] **300** [15]
Total Dissolved Solids (TDS) Present in Make-up Water in Various Studies	**133,900** [1] 110,304[3]	**>300,000** [7] 273,552 [8] 222,232 [9] 22,906 [10]	50,000[11] 126,128 [12] 241,354 [13] 157,916 [14] 110,000 [15] 33,100 [16] **273,828** [17] 236,840 [18] 77,460 [19] 258,333 [20]
Temperature	BHSTs to 300ºF [5] Less than 200ºF [6]	Up to 350ºF [2] BHSTs to 375ºF [5]	---
Fluid pH in Various Studies	9-12 [1] 9-10 [2] **8.5-12** [3] 9.5-10.5 [4] 9-12 [5]	**4-10** [5] 5.12 [7] 8 [8] 5.73 [9] 5.5 [10]	7 to 7.5 [11] 6.4 [12] 6.02 [13] 7-8 [14] 5.4 [15] 8.06 [16] 4.45-5.43 [17]
Cation			
Monovalent Cation Concentration Present in Make-up Water in Various Studies	**44,050** [1] 42,417 [3]	76,232 [7] **77,206** [8] 69,167 [9] 9,719 [10]	43,034 [12] 73,978 [13] 49,803 [14] 24,190 [15] 7,028 [16] **94,087** [17] 52,519 [18] 27,977 [19] 88,281 [20]
Sodium Cation Concentration Present in Make-up Water in Various Studies	**42,700** [1] 39,321 [3] 3,000 [4]	**75,720** [7] 75,517 [8] 68,692 [9] 4,719 [10]	43,034 [12] 73,978 [13] 49,803 [14] 24,190 [15] 20,200 [16] **88,690** [17] 52,519 [18] 27,479 [19] 88,281[20]

Table 6 continued…

Cation continued			
Potassium Cation Concentration Present in Make-up Water in Various Studies	1,350 [1] **3,096** [3] 2,000 [4]	512.3 [7] 1,689 [8] 475 [9] **5,000** [10]	512 [14] 190 [15] 2,290 [16] 5,5397 [17] **17,820** [18] 498 [19]
Divalent Cation Concentration Present in Make-up Water in Various Studies	**8,480** [1] 5,093 [3]	17,081[7] **34,019** [8] 29,128 [9] 157 [10]	5,479 [12] 17,315 [13] 10,500 [14] 17,399 [15] 24,090 [16] **46,230** [17] 36,921 [18] 2,003 [19] 17,227 [20]
Calcium Cation Concentration Present in Make-up Water in Various Studies	**6,120** [1] 1,326 [3] 200 [4]	14,750 [7] **28,845** [8] 13,200 [9] 137 [10]	4,332 [12] 12,313 [13] 10,500 [14] 11,000 [15] 148 [16] 27,900 [17] **33,920** [18] 1,038 [19] 13,900 [20]
Barium Cation Concentration Present in Make-up Water in Various Studies	**0-1.1** [3]	**7.63** [7] 6.03 [8] 5 [9]	<20 [11] 2,900 [15] **9,800** [17] 1,454 [18] 2 [20]
Magnesium Cation Concentration Present in Make-up Water in Various Studies	**1,790** [1] 912 [3] 400 [4]	1,263 [7] **3,148** [8] 2,433 [9] 20 [10]	1,097 [12] 4,992 [13] <940 [15] 1,470 [17] 1,269 [18] 965 [19] **5,372** [20]
StrontiumCation Concentration Present in Make-up Water in Various Studies	**1,800** [1] 363 [3]	951.8 [7] **2,020** [8]	2,300 [15] **6,970** [17] 1,237 [18]

Table 6 continued…

Cation continued			
Iron Cation Concentration Present in Make-up Water in Various Studies	**0.4** [3]	**109.2** [7] 0.264 [8] 15 [9]	<10[11] 50 [12] 10 [13] 4 [14] <75 [15] 95 [17] **156** [18] 75 [20]
BoronCation Concentration Present in Make-up Water in Various Studies	**27** [3]	**500** [7] 16.6 [8] 21 [9]	**334** [17]
SilicaCation Concentration Present in Make-up Water in Various Studies	**2.3** [3]	**80** [9]	---
Anion			
Chloride Anion Concentration Present in Make-up Water in Various Studies	**81,000** [1] 67,000 [3]	153,861[7] **164,951** [8] 136,750 [9] 10,100 [10]	76,715[12] 149,750 [13] 100,000 [14] 66,750 [15] 6,880[16] **165,500** [17] 147,400 [18] 47,480 [19] 160,000 [20]
Sulfate Anion Concentration Present in Make-up Water in Various Studies	**3,300** [1] 3,053 [3]	580[7] 38 [8] 615 [9] **2,000** [10]	399 [12] 250 [13] **3,053** [14] 3 [15] 1,600 [16] 282 [17] 220 [18] 26 [20]
Carbonate Anion Concentration Present in Make-up Water in Various Studies	**40** [1]	1 [9] **240** [10]	**108** [16]
Bicarbonate Anion Concentration Present in Make-up Water in Various Studies	**370** [1] 335 [3]	48.8 [7] 51 [9] **691** [10]	551 [12] 61 [13] 177 [14] **1,870** [16] 127 [17] 189 [18]

Table 6 continued…

Hardness (CaCO3) Present in Make-up Water in Various Studies	---	30,000 [7] **42,981 [9]**	51,581 [13] **75,726 [17]**

[1] Harris et al., 1999
[2] Ainley et al., 1993
[3] Monreal et al., 2014
[4] Haghshenas et al., 2014
[5] Brannon, 2010
[6] Cameron. et al., 1989
[7] Kakadhian et al., 2013
[8] Lebas et al., 2013
[9] Zhou et al., 2013
[10] Huang et al., 2005
[11] King, 2012
[12] Zelenev et al., 2009
[13] Zhou et al., 2014
[14] Tucker et al., 2014
[15] Ferguson et al., 2013
[16] Rimassa et al., 2009
[17] Gupta et al., 2012
[18] Kolla et al., 2013
[19] Paktinat et al., 2011
[20] Fontenelle et al., 2013

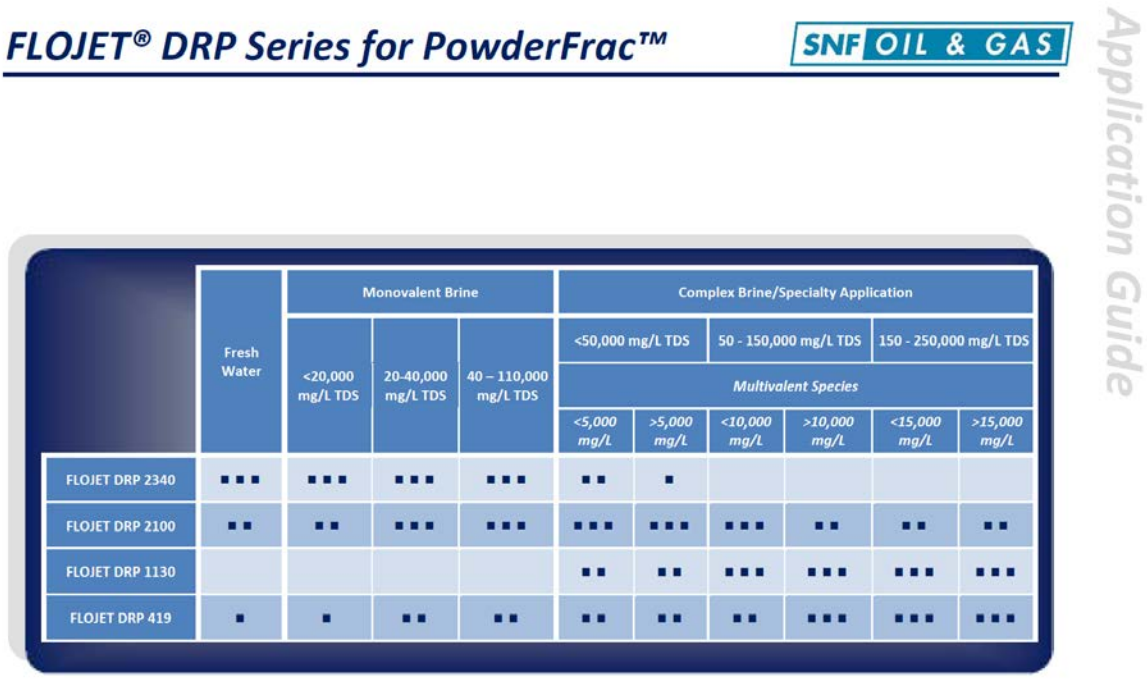

Figure 12 - Application Guide for FLOJET DRP Series for PowderFrac of SNF

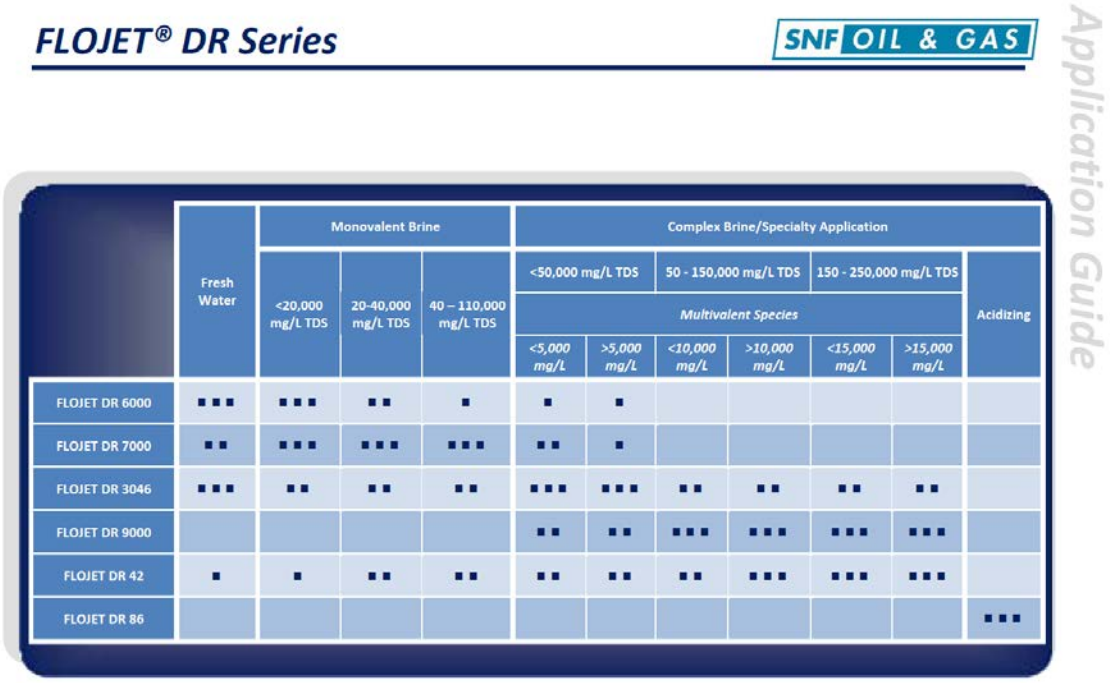

Figure 13 - Application Guide for FLOJET DR Series of SNF

Table 7 – Water composition of non-potable groundwater from the Southern Carrizo-Wilcox aquifer

Contents	Min	P10	P50	P90	Max	Mode
TDS	1,001	1,044	1,397	3,060	25,206	1026
pH	4.30	7.02	7.89	8.60	9.00	7
Sodium	31	185	452	1,010	9,626	405
Potassium	1	2	5	15	134	1
Calcium	1	2	10	288	988	1
Barium *	0	0	0	0	34	0
Magnesium	0	1	4	83	513	1
Strontium	0	0	1	3	12	0
Iron *	1	1	2	10	368	0
Boron *	0	0	0	1	6	0
Chloride	22	158	352	1,055	15,050	170
Sulfate	0	1	125	722	3,092	0
Carbonate	0	0	0	24	170	0
Bicarbonate	0	217	560	1,226	2,510	249
Hardness (CaCO3)	2	7	41	990	3,757	4
Depth (ft)	15	70	607	3,200	6,211	150

* Barium, Iron, and Boron data take into account of all groundwater samples from the entire Carrizo-Wilcox aquifer

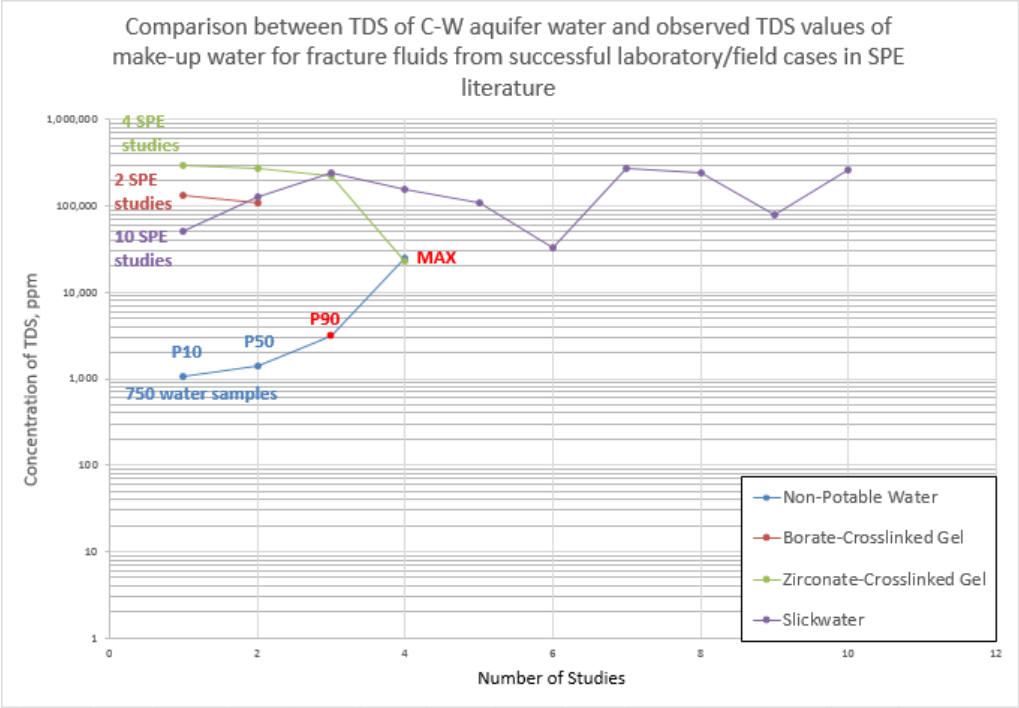

Figure 14– TDS comparison between S C-W aquifer groundwater and water samples from successful case studies in SPE literature

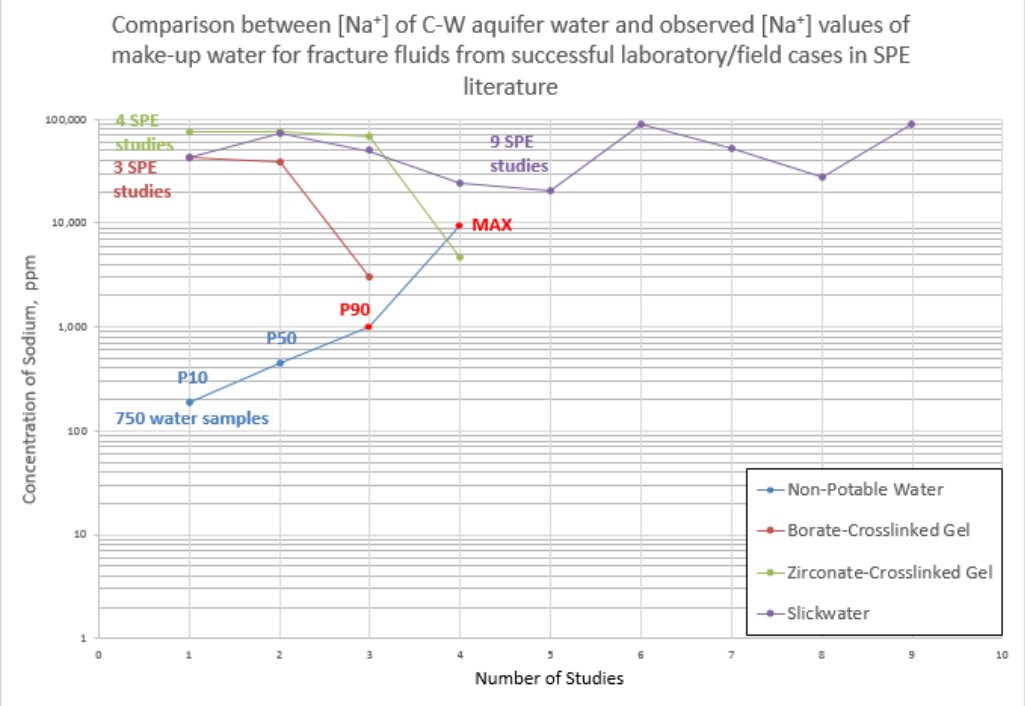

Figure 15 – Sodium comparison between S C-W aquifer groundwater and water samples from successful case studies in SPE literature

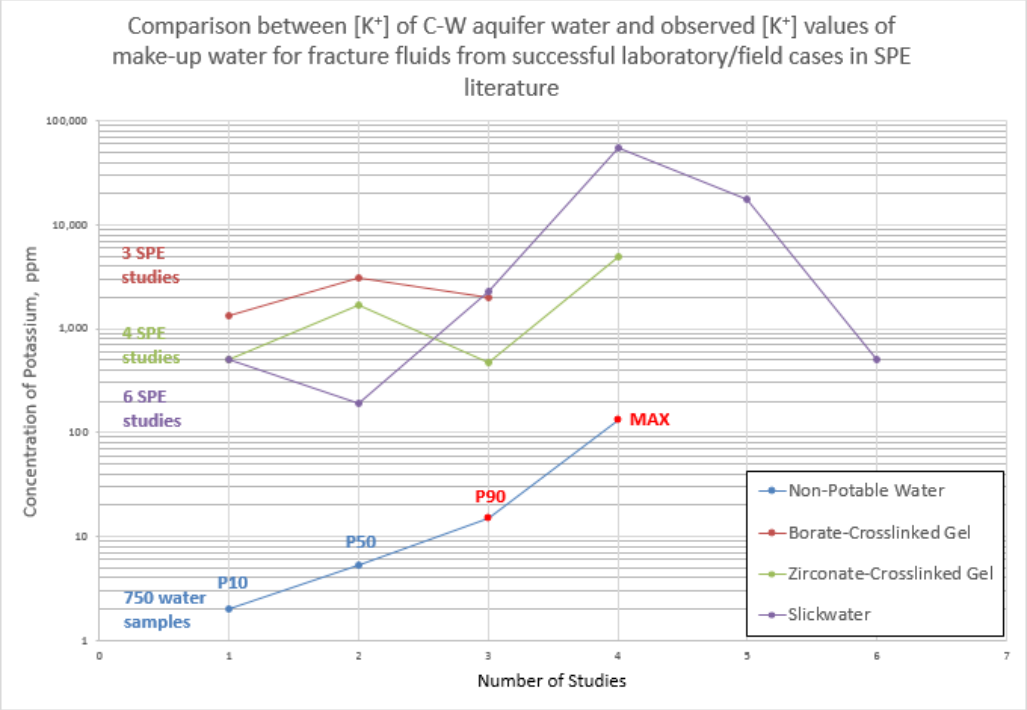

Figure 16 – Potassium comparison between S C-W aquifer groundwater and water samples from successful case studies in SPE literature

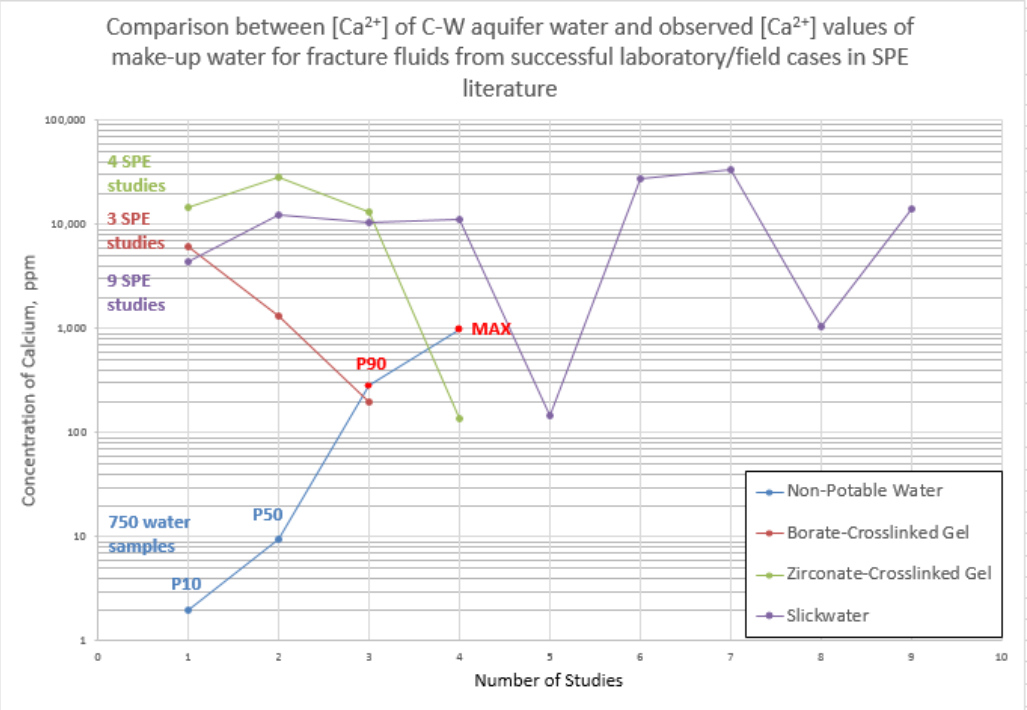

Figure 17 – Calcium comparison between S C-W aquifer groundwater and water samples from successful case studies in SPE literature

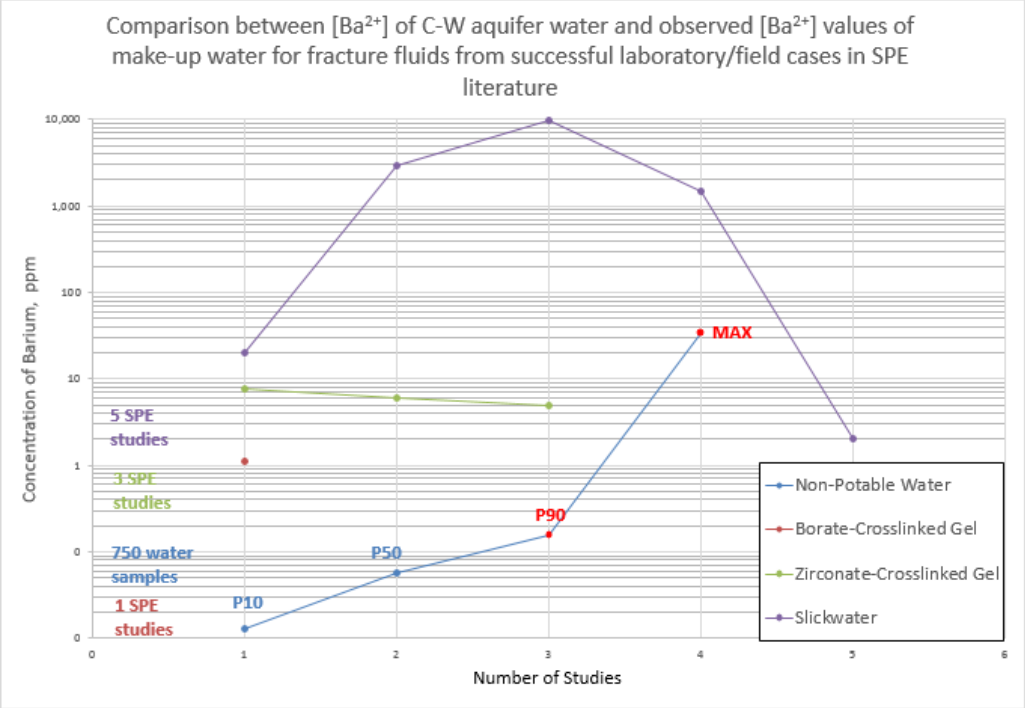

Figure 18 – Barium comparison between S C-W aquifer groundwater and water samples from successful case studies in SPE literature

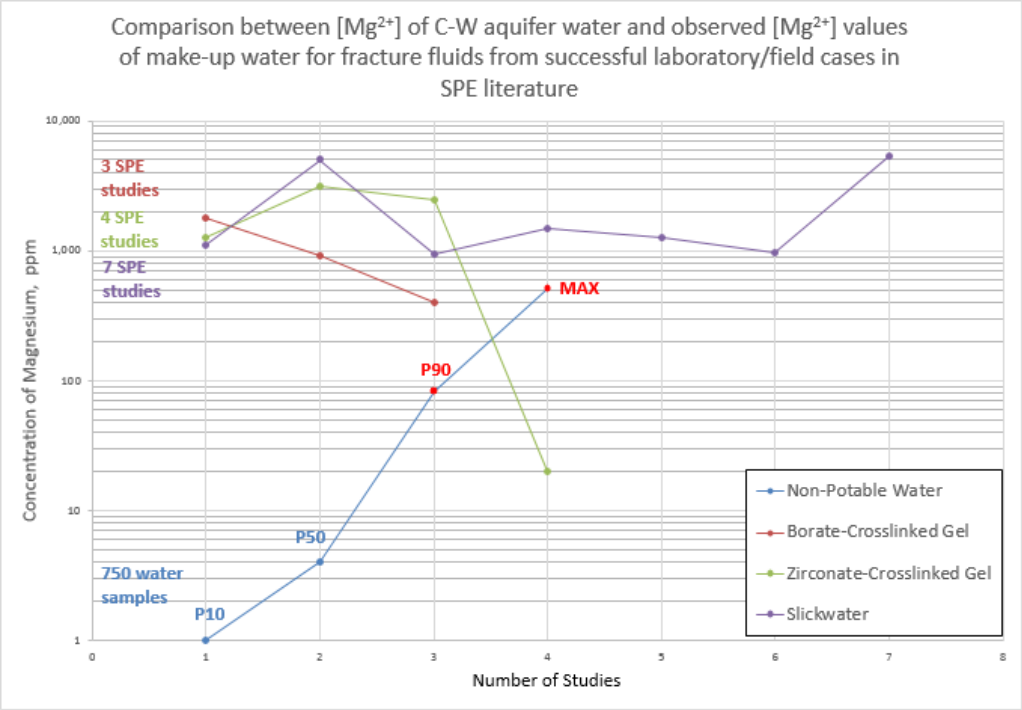

Figure 19 – Magnesium comparison between S C-W aquifer groundwater and water samples from successful case studies in SPE literature

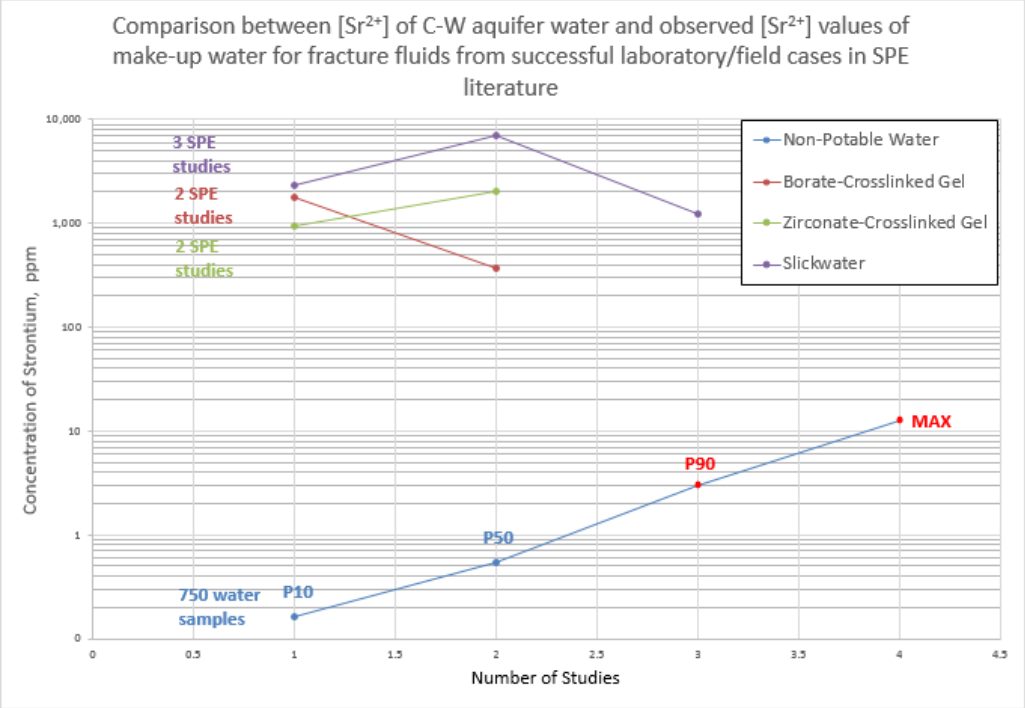

Figure 20 – Strontium comparison between S C-W aquifer groundwater and water samples from successful case studies in SPE literature

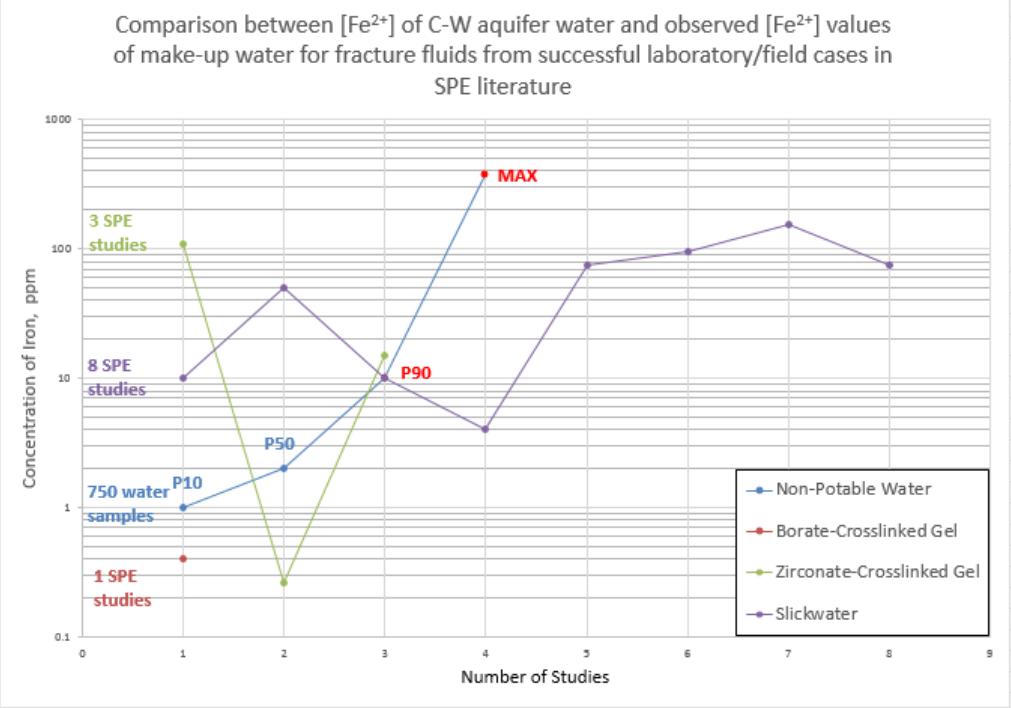

Figure 21 – Iron comparison between S C-W aquifer groundwater and water samples from successful case studies in SPE literature

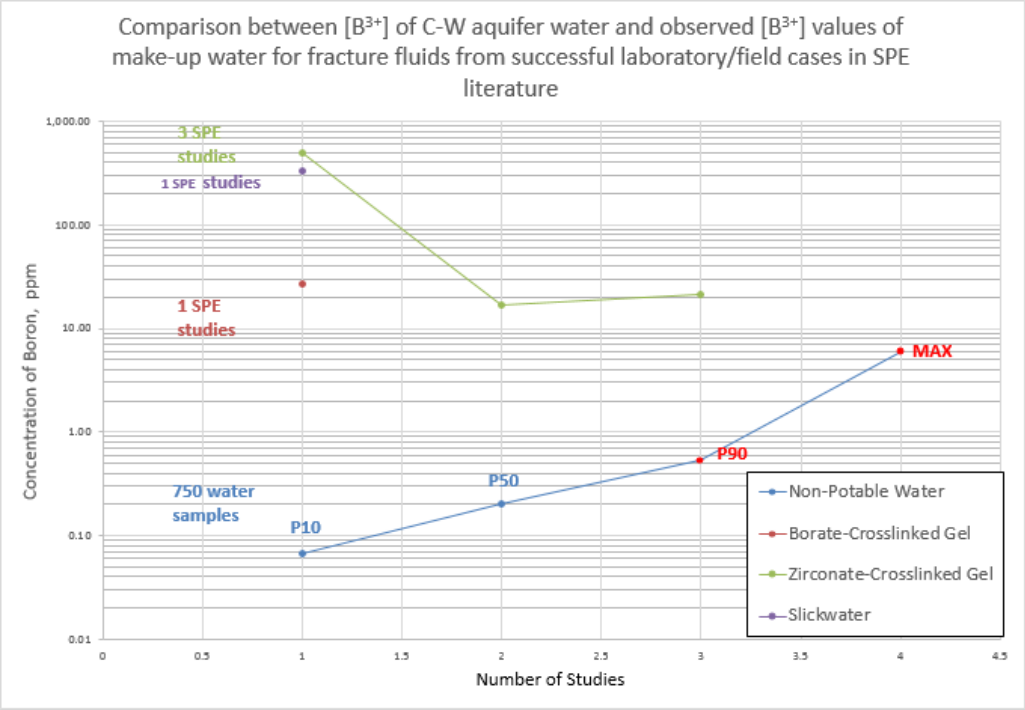

Figure 22 – Boron comparison between S C-W aquifer groundwater and water samples from successful case studies in SPE literature

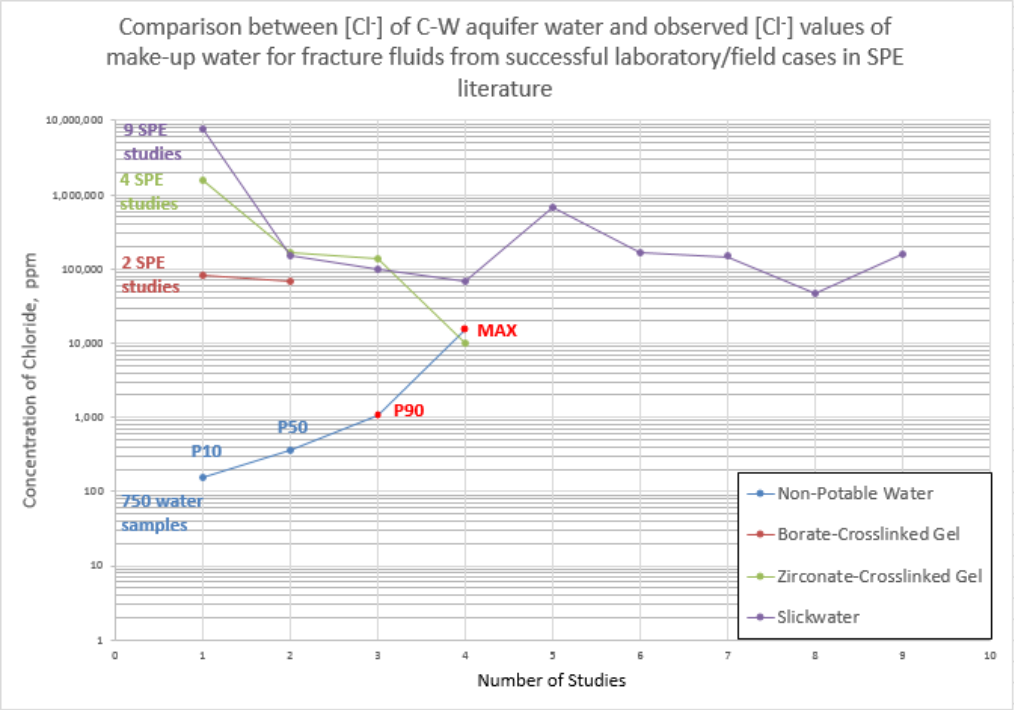

Figure 23 – Chloride comparison between S C-W aquifer groundwater and water samples from successful case studies in SPE literature

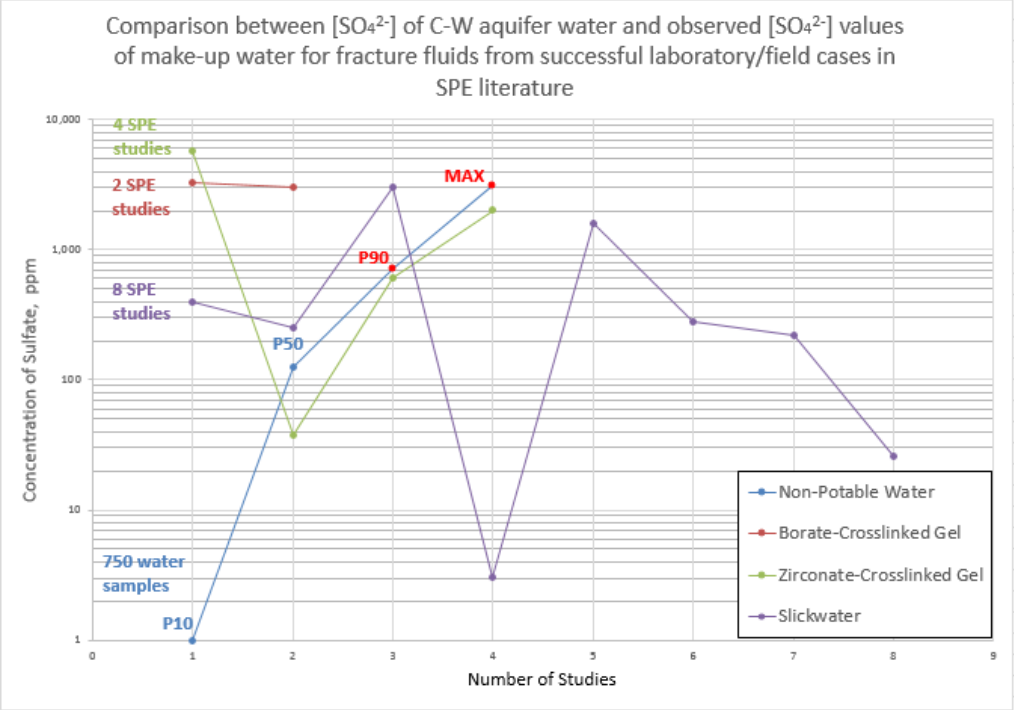

Figure 24– Sulfate comparison between S C-W aquifer groundwater and water samples from successful case studies in SPE literature

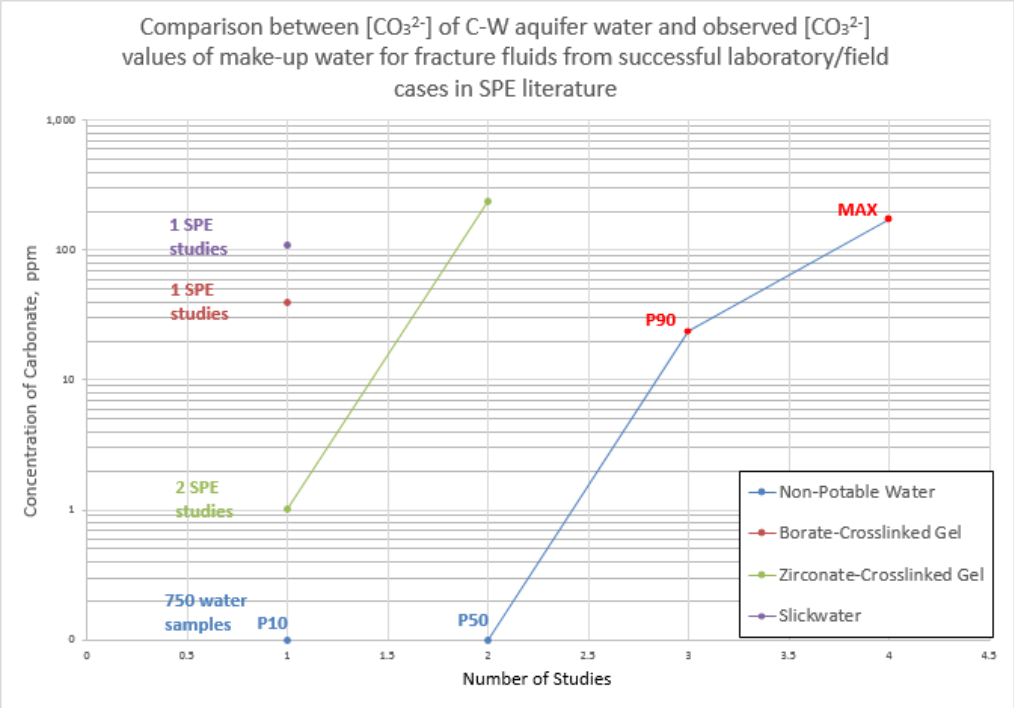

Figure 25– Carbonate comparison between S C-W aquifer groundwater and water samples from successful case studies in SPE literature

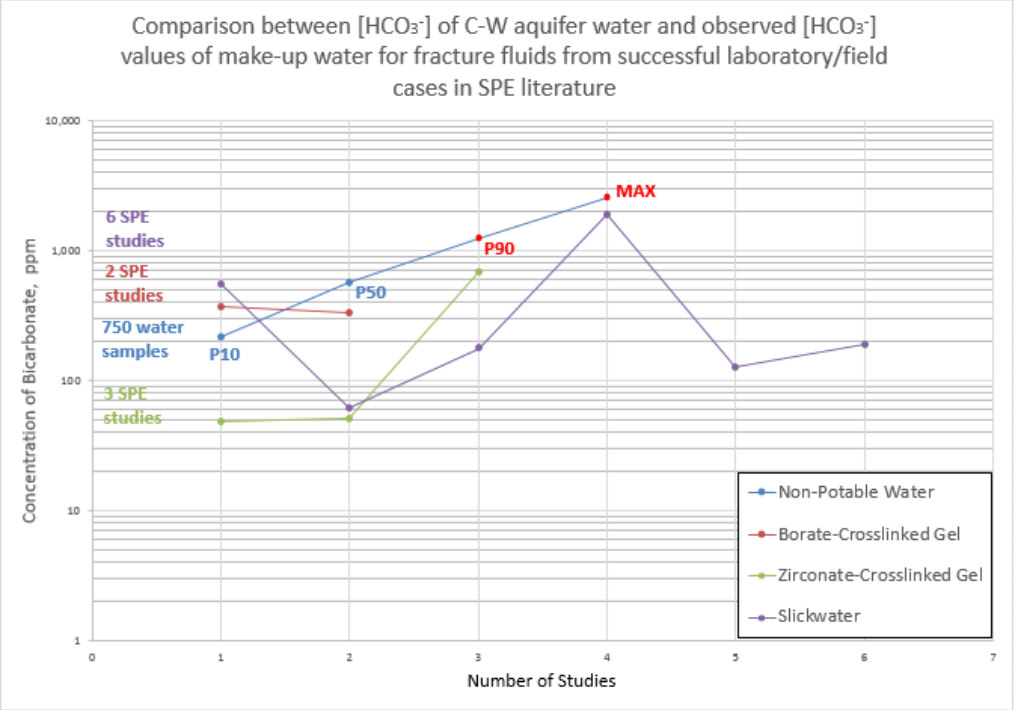

Figure 26– Bicarbonate comparison between S C-W aquifer groundwater and water samples from successful case studies in SPE literature

Table 8 – The performance of friction reducer in fresh water and saline water

Cases	Friction Reduction, %			
	Trial 1	Trial 2	Trial 3	Average
Fresh Water	32.49	32.72	32.39	32.53
Synthetic Saline Water [TDS of greater than 29,577 ppm, max. concentration of all ions, and 10 ppm of Fe]	29.3	30.32	29.3	29.64

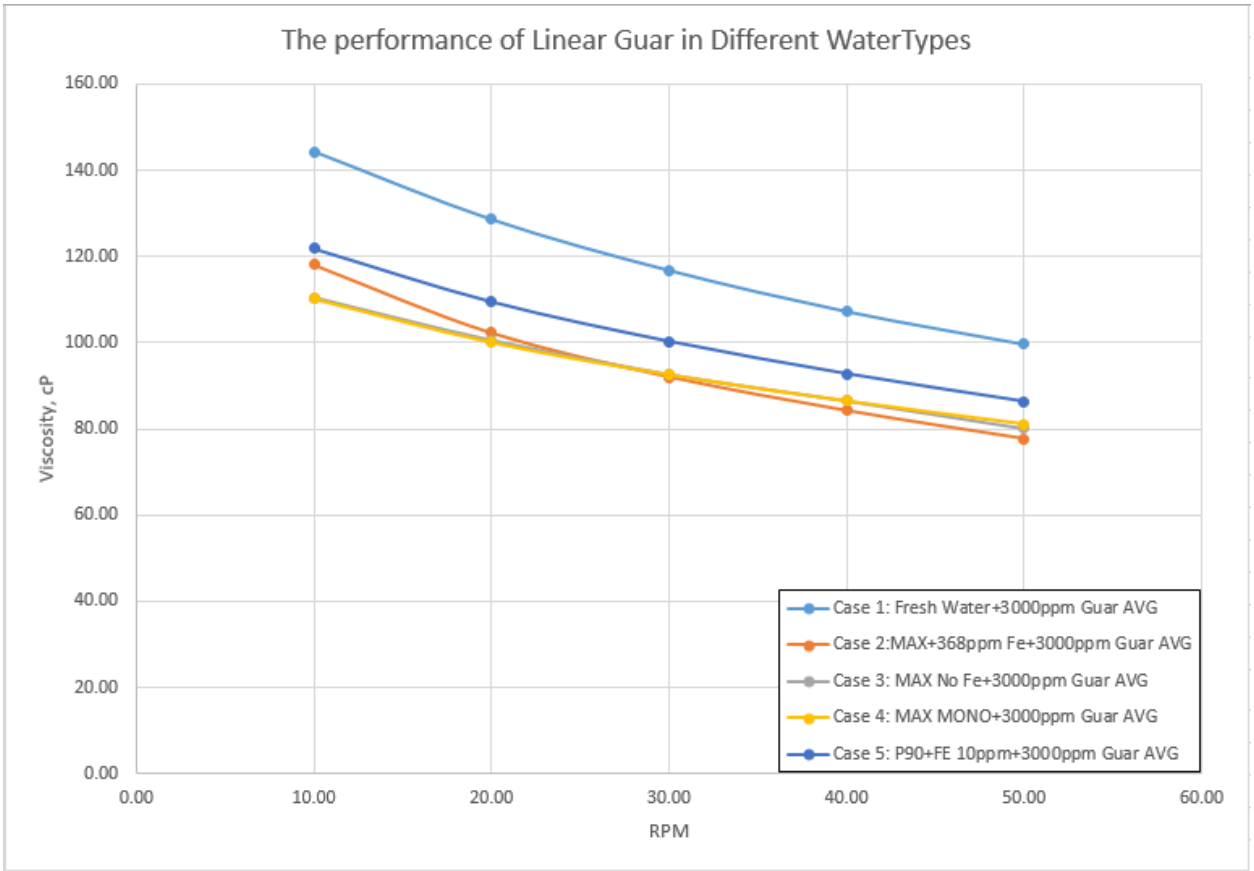

Figure 27 – The performance of linear guar in different water types

Table 9 – The performance of borate-crosslinked guar gel in different water types

Cases	Lipping Test	Gel Strength
Case 1: TDS of 250-500 ppm	Pass	Strong
Case 2: TDS of greater than 30,617 ppm	Fail	N/A
Case 3: TDS of greater than 29,548 ppm	Fail	Very weak
Case 4: TDS of greater than 24,726 ppm	Pass	Strong
Case 5: TDS of greater than 3,824 ppm	Pass	Strong
Case 6: TDS of greater than 29,548 ppm	Pass	Very Strong

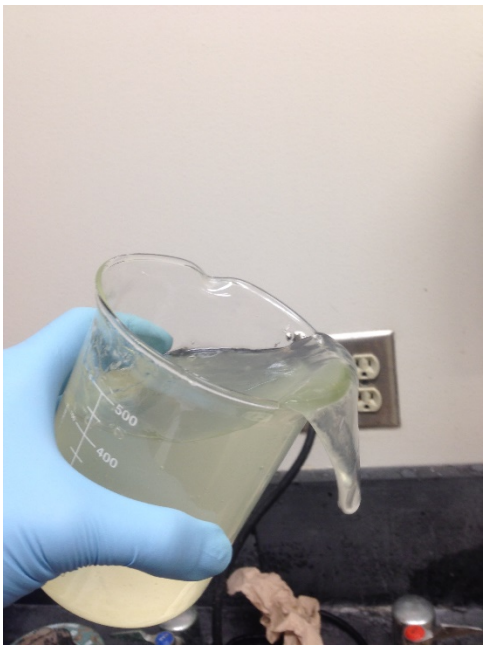

Figure 28 – Lipping test success of borate-crosslinked guar gel using 3000ppm guar and fresh water – Case 1

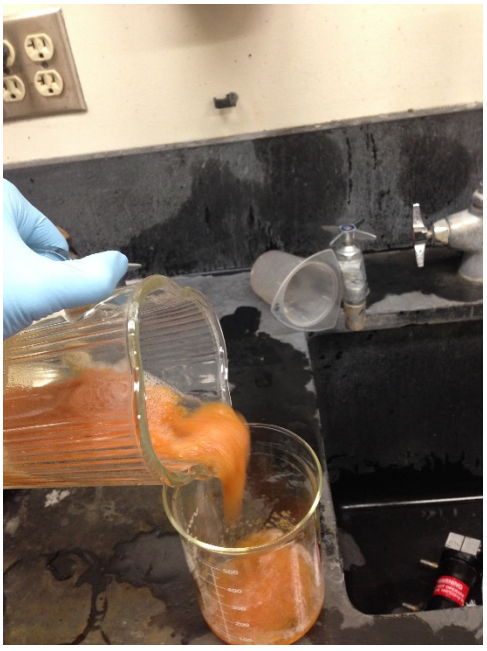

Figure 29 – Lipping test failure of borate-crosslinked guar gel using 3000ppm guar and saline water with the maximum ion concentration (including 368 ppm Iron) – Case 2

Figure 30 – Lipping test failure of borate-crosslinked guar gel using 3000ppm guar and saline water with the maximum ion concentration (excluding Iron) – Case 3

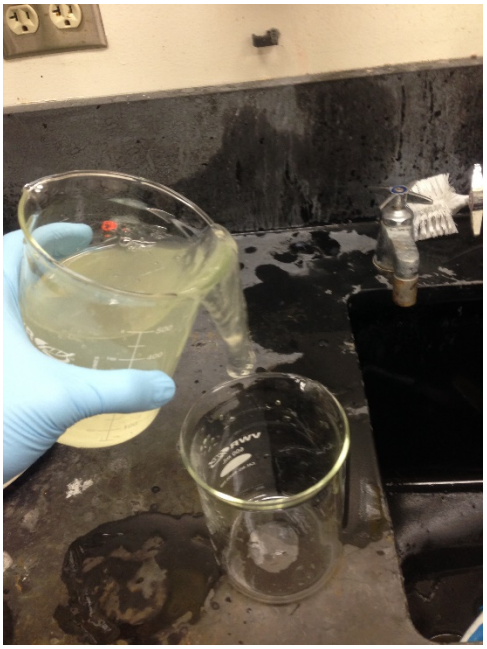

Figure 31– Lipping test success of borate-crosslinked guar gel using 3000ppm guar and saline water containing only monovalent ions with the maximum concentration – Case 4

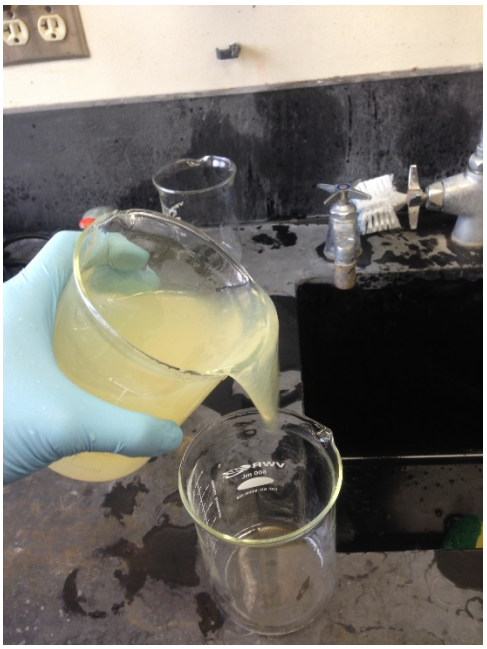

Figure 32 – Lipping test success of borate-crosslinked guar gel using 3000ppm guar and saline water with P90 values of all ion concentration (including 10 ppm Iron) – Case 5

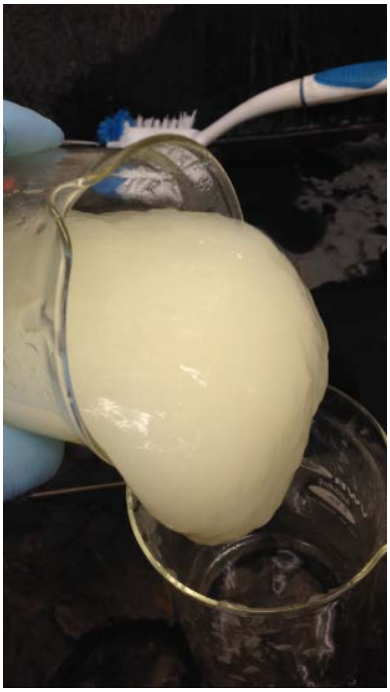

Figure 33 – Lipping test success of borate-crosslinked guar gel using 6000ppm guar and saline water with the maximum ion concentration (excluding Iron) – Case 6